

MEMBRANE TREATMENT OF AQUEOUS FILM FORMING
FOAM (AFFF) WASTES FOR RECOVERY OF
ITS ACTIVE INGREDIENTS

FINAL REPORT

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by

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ABSTRACT

→ Ultrafiltration (UF) and Reverse Osmosis (RO) treatment of Aqueous Film Forming Foam (AFFF) solutions was investigated to determine the feasibility of employing membrane processes to separate and recover AFFF active ingredients for reuse. Studies were performed on both 6% AFFF in tap-water solutions and on actual wastewaters spiked with 3% or 6% AFFF.

The AFFF materials used in this study consisted of Ansul, 3M FC-206, and 3M FC-780. Membranes employed for these studies included Abcor HFD, HFF, HFJ, and HFK tubular ultrafiltration (UF) membranes and a DuPont B-10 reverse osmosis (RO) module. Parameters monitored to represent AFFF ingredients were TOC, dissolved solids, surfactants, and % glycol. An attempt was also made to determine fluorocarbons as fluoride. Membrane fluxes were also determined.

Results of this study demonstrate the feasibility of employing UF-RO processes to separate and recover the AFFF active ingredients for reuse. Approximately 75% recovery of the AFFF active ingredients as represented by the foam test was attained. An economic analysis of the membrane treatment processes indicates that it is extremely favorable in recovering the AFFF wastewater for reuse. Pilot-scale studies are, however, necessary to fully establish the process feasibilities and economics of the AFFF recovery system.

SUMMARY

Ultrafiltration (UF) and Reverse Osmosis (RO) treatment of Aqueous Film Forming Foam (AFFF) solutions was investigated to determine the feasibility of employing membrane processes to separate and recover AFFF active ingredients for reuse. Studies were performed on both 6% AFFF in tap-water solutions and on actual wastewaters spiked with 3% or 6% AFFF.

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TABLE OF CONTENTS

	Page
REPORT DOCUMENTATION	i
SUMMARY	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vi
LIST OF ILLUSTRATIONS	ix
I. INTRODUCTION	1
Statement of the Problem	
Objective of Research	
Review of the Literature	
II. MATERIALS	17
Chemicals	
Type of Wastewaters	
Experimental Set-Up	
System and Equipment Design for	
Ultrafiltration	
System and Equipment Design for	
Reverse Osmosis	
III. EXPERIMENTAL PROCEDURE	29
Determine the Optimum Operating Conditions	
Ultrafiltration	
Reverse Osmosis	
Feasibility Studies to Separate and Concen-	
trate AFFF	
Characterization of AFFF Constituents	
Surfactants	
Glycols	
Fluorocarbons (as Fluoride)	
Gross Parameters	

IV. RESULTS AND DISCUSSION	40
Characterization of AFFF Concentrates	
Characterization of Wastewaters from	
Fire Fighting Training Exercise	
Wastewaters	
Membrane Processes	
First Phase Experiment with 6% AFFF	
Tap-Water Study	
Second Phase Experiment with 3% AFFF	
Spiked Wastewater	
Third Phase Experiment with 6% AFFF	
Tap-Water	
Fourth Phase Experiment with 6% AFFF	
Spiked Wastewaters	
V. PROCESS ECONOMICS	90
VI. CONCLUSIONS	94
VII. RECOMMENDATIONS	96
REFERENCES	98
APPENDIX.	100
I. Commercial Applications of Membrane Process. .	101
II. Quotation of a 50,000 GPD UF System	102

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LIST OF TABLES

Table	Page
1. Difference between Reverse Osmosis and Ultrafiltration	6
2. Permasep Permeator Model No. 6440-015 Product Specifications	27
3. DuPont B-10 RO Module Performance Study	33
4. Analysis of AFFF Concentrates	41
5. Characterization of Fire Fighting Training Exercise Wastewater (San Diego)	44
6. Characterization of Fire Fighting Training Exercise Wastewater (Warner-Robbins Air Force Base)	45
7. Relationships between VCR, VRR, and PWR	47
8. Overall Rejection of HFD and HFF Ultrafiltration Membranes Study with 6% AFFF Tap-Water Solution	48
9. Results of Membrane Study with 6% Ansul Solution with HFD and HFF Ultrafiltration Membranes (@ 25°C run)	50
10. Results of Membrane Study with 6% 3M FC-206 Solution with HFD and HFF Ultrafiltration Membranes (@ 25°C run)	51
11. Results of Membrane Study with 6% 3M FC-780 Solution with HFD and HFF Ultrafiltration Membranes (@ 25°C run)	52
12. Results of DuPont Reverse Osmosis B-10 Module Study with Various 6% AFFF Solution from Ultrafiltration Permeate	53
13. Results of HFD and HFF Ultrafiltration Membranes Study with 3% Ansul Spiked Fire Fighting Training Exercises Wastewater from San Diego (@ 25°C run)	54
14. Results of HFD and HFF Ultrafiltration Membranes Study with 3% 3M FC-206 Spiked Fire Fighting Training Exercises Wastewater from San Diego (@ 25°C run)	55

15.	Results of DuPont Reverse Osmosis B-10 Module Study with Various 3% AFFF Spikes Fire Fighting Training Exercises Wastewater Solution from Ultrafiltration Permeate	57
16.	Results of Membrane Study with 6% Ansul Solution with HFJ and HFK Ultrafiltration Membranes (@ 25°C run)	62
17.	Results of Membrane Study with 6% Ansul Solution with HFJ and HFK Ultrafiltration Membranes (@ 50°C run)	63
18.	Results of Membrane Study with 6% 3M FC-206 Solution with HFJ and HFK Ultrafiltration Membranes (@ 25°C run)	64
19.	Overall Rejections of HFJ and HFK Ultrafiltration Membranes Study with 6% AFFF Tap-Water Solution	68
20.	Results of Membrane Study with 6% Ansul Solution from UF Permeate	70
21.	Results of Membrane Study with 6% 3M FC-206 Solution from Ultrafiltration Permeate	71
22.	Results of Reverse Osmosis Study with 6% AFFF Solution from Ultrafiltration Permeate	72
23.	Performance of Ultrafiltration and Reverse Osmosis Processed in Treating 6% AFFF Spiked Fire Fighting Exercise Wastewater from Warner-Robbins Air Force Base	78
24.	Results of HFJ and HFK Ultrafiltration Membranes Study with 6% Ansul Spiked Fire Fighting Training Exercises Wastewater from Warner-Robbins Air Force Base (@ 50°C run)	79
25.	Results of HFJ and HFK Ultrafiltration Membranes Study with 6% 3M FC-206 Spiked Fire Fighting Training Exercises Wastewater from Warner-Robbins Air Force Base (@ 50°C run)	80
26.	Results of DuPont Reverse Osmosis B-10 Module Study with 6% Ansul Spiked Fire Fighting Training Exercise Wastewater Solution from UF Permeate	87

27.	Results of DuPont Reverse Osmosis B-10 Module Study with 6% 3M FC-206 Spiked Fire Fighting Training Exercises Waste- water Solution from Ultrafiltration Permeate	88
28.	Estimated Capital and Operation Cost of the Proposed Membrane Treatment System (Figure 28)	92

LIST OF ILLUSTRATIONS

Figure		Page
1.	Simplifier Flow Schematic of Ultrafiltration and Reverse Osmosis (1)	5
2.	Comparison of Flow Schemes in Reverse Osmosis and Ultrafiltration	7
3.	Concentration Polarization Schematic	14
4.	Concentration Profile near the Membrane Surface at Steady-State Conditions	14
5.	Batch Operation of an Ultrafiltration System . . .	19
6.	Continuous Feed and Bleed Operation of an Ultrafiltration System	20
7.	A Schematic Diagram of the Ultrafiltration Pilot-Plant	21
8.	Cut-Away View of a Tubular Ultrafiltration Assembly	23
9.	A Schematic Diagram of the Reverse Osmosis Pilot-Plant	25
10.	Cut-Away View of a Permasep Permeator Reverse Osmosis Assembly	28
11.	Abcor HFJ and HFK Ultrafiltration Membranes Pressure Effect Tap-Water Studies	30
12.	Abcor HFJ and HFK Ultrafiltration Membranes Temperature Effect Tap-Water Studies	32
13.	Effect of Temperature on Ultrafiltration Membrane Flux (6% Ansul Solution with Tap-Water)	59
14.	Ultrafiltration Membrane Performance (6% 3M FC-206 Solution with Tap-Water)	60
15.	Ultrafiltration Membrane Performance of Ansul Constituents Transport at 25°C Run (6% Ansul Solution with Tap-Water)	65
16.	Ultrafiltration Membrane Performance of Ansul Constituents Transport at 50°C Run (6% Ansul Solution with Tap-Water)	66

17.	Ultrafiltration Membrane Performance of 3M FC-206 Constituents Transport at 25°C Run (6% 3M FC-206 Solution with Tap- Water)	67
18.	Reverse Osmosis Performance as a Function of Product Water Recovery (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study) . .	73
19.	Relationships between Reverse Osmosis Con- centrate and Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study)	74
20.	Reverse Osmosis Performance of AFFF Constituents Present in the Permeate as a Function of Volu- metric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study) . .	75
21.	Reverse Osmosis Performance of AFFF Constituents Present in the Permeate as a Function of Volu- metric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study) . .	76
22.	Ultrafiltration Membrane Performance of AFFF Constituents Transport (6% AFFF Spiked Waste- water)	81
23.	Ultrafiltration Membrane Flux as a Function of Product Water Recovery (6% AFFF Spiked Wastewater)	33
24.	Relationships between Reverse Osmosis Concentrate and Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% AFFF Spiked Wastewater)	84
25.	Reverse Osmosis Performance of AFFF Constituents Present in the Permeate as a Function of Volu- metric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% AFFF Spiked Waste- water)	85
26.	Reverse Osmosis Performance of AFFF Constituents Present in the Permeate as a Function of Volu- metric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% AFFF Spiked Wastewater) .	86

27. Reverse Osmosis Performance as a Function
of Product Water Recovery (Feed Solution
from 6% AFFF Spiked Wastewater) 89
28. Proposed Membrane Treatment System for AFFF
Wastewater 91

I. INTRODUCTION

Statement of the Problem

Waste streams generated by fire fighting training exercises at military installations contain fire fighting agents, residual fuel oil, combustion products, and suspended solids. Such agents are commonly referred to as Aqueous FilmForming Foam (AFFF) which contain fluorocarbons, hydrocarbon surfactants, solvents (such as various glycols) and water. During fire fighting exercises and equipment function tests, a 6% solution of AFFF concentrate is used alone or in combination with Purple K Powder (potassium bicarbonate).

All of the constituents resulting from fire fighting exercises are considered to have adverse effects environmentally. Toxicity studies of AFFF wastewaters have been reported to result in a 48-hour TLm of 150 ppm (V/V) to oyster larvae when discharged to the aquatic environment (5). The organic constituents present in AFFF have been reported to resist biodegradation in conventional biological processes as well as contributing to operational problems (5). Research efforts, therefore, have been directed towards developing an effective method for treating this wastewater.

Membrane processes are one group of promising physico-chemical processes in the treatment of AFFF wastewater (7). Chian (7) demonstrated that all the active ingredients of AFFF concentrate were rejected well by a DuPont B-10 hollow fiber permeator. Also, most of these ingredients readily passed

ultrafiltration membranes. It is therefore quite probable that a membrane treatment scheme may be developed to economically recover the AFFF active ingredients from a waste stream. This recovered material might then be reused either alone or supplemented with virgin AFFF concentrate. Such a process would result in a considerable cost saving because of the high cost of AFFF chemical agents and the large quantity of these agents used each year. The present research effort is directed toward examining the effectiveness of ultrafiltration and reverse osmosis treatment for the separation and recovery of AFFF active ingredients. Samples of recovered AFFF solutions were field tested by Mr. H. Peterson at the Naval Research Laboratory, Washington, D.C. to determine the suitability of the recovered solutions for reuse. The results of these tests are positive.

Research Objectives

Wastewater generated from fire fighting exercises have an adverse effect upon the receiving stream and resist biodegradation in conventional biological process whereas, the fire fighting agent (AFFF concentrate) itself is a very costly material (5). This leads to the idea that reclamation and reuse of AFFF concentrate may prove to be the most economical solution to the problem of treatment and disposal of waste streams generated from AFFF fire fighting training exercises.

The objectives of this study were:

1. to develop standard analytical methods for the determination of the specific constituents in AFFF fire fighting solution and the resulting wastewater;
2. to investigate the possibility of recovering the active ingredients in the AFFF solution for reuse;
3. to investigate the possibility of improving the membrane treatment scheme by selection of membrane type and characteristics; and
4. to investigate the particulars of membrane treatment of wastewater generated from fire fighting exercises.

Review of the Literature

Membranes in Separations

Membranes can be interspersed between phases: gas, liquid or solid. The separate phenomena are different from ordinary filtration; they depend not only on the physical properties of both the membrane and the solute, but also on the chemical characteristic which constitutes one of the major parameters affecting the membrane separation process (8,16,18,20). Membrane processes are usually a matter of choice from the point of view of efficiency and cost, particularly when thermally unstable or biologically active materials are involved, or when a large volume of dilute solutions is to be processed (18).

The primary interest in this research and the purpose of this literature review are to focus on the fluid-solid systems. Ultrafiltration and reverse osmosis separation techniques will be examined. Based on negative or positive sorption (or preferential sorption) of substances at fluid-solid interfaces, and under pressure through appropriate semi-permeable membrane (20). The constituents in the feed streams pass over the membrane, diffuse through it, and finally leave the membrane from the other side.

Previous works (8,18,20) indicated that no single equipment design of membrane configuration will be optimum for all applications. Feasibility studies or design for each application requires a basic body of experimental data. The engineering science of membrane transport processes is concerned with the development of the basic transport equations and the

integration of the physicochemical parameters governing separations into such basic equations (20). This leads to the development of precise analytical techniques of membrane specification, prediction of membrane performance, analysis and design of membrane processes, application of membrane separation, concentration, and fractionation of substance under a wide variety of experimental conditions. From an engineering point of view, flux, semipermeability, and mechanical strength are the fundamental criteria and remain the cornerstone in research and development (11). Understanding of the basic transport process is important and will be examined thoroughly.

Differences between Reverse Osmosis (RO) and Ultrafiltration (UF)

Reverse osmosis and ultrafiltration processes were similar in that the hydraulic pressure is used as the driving force, and a synthetic semi-permeable membrane is employed as the separating medium. The processes have a unique aspect that they do not involve a phase change of any interfacial mass transfer, as shown in Figure 1.

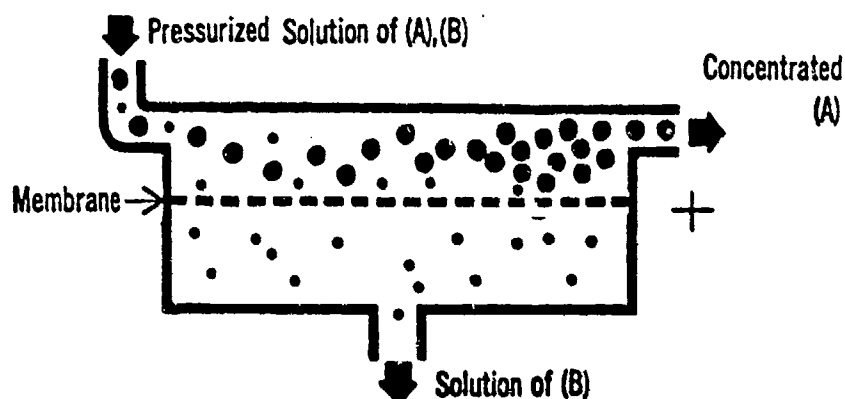


Figure 1. Simplified flow schematic of UF and RO (1)

The major difference between ultrafiltration and reverse osmosis are mainly in the mechanisms of solute transport applications, process conditions and equipment required for the two processes. Some of the important differences are presented in Table 1 (12). Figure 2 illustrates the flow schemes for the two processes (1).

Table 1
Differences Between Reverse Osmosis and Ultrafiltration

	<u>Reverse Osmosis</u>	<u>Ultrafiltration</u>
Size of solute retained	Molecular weights generally much less than 500, e.g., 150	Molecular weights generally over 1000
Osmotic pressures of feed solutions	Important, can range to over 68.05 atm	Generally negligible
Operating pressures	Greater than 6.81 atm up to 136.1 atm	0.68 to 6.81 atm
Nature of membrane retention	Diffusive transport barrier; possibly molecular screening	Molecular screening
Chemical nature of membrane	Important in affecting transport properties	Unimportant in affecting transport properties so long as proper size distribution are obtained

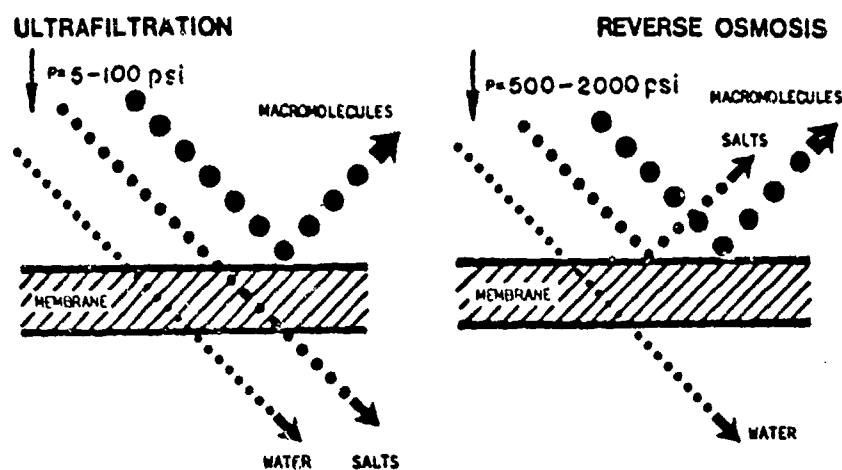


Figure 2. Comparison of flow schemes in Reverse Osmosis and Ultrafiltration (1)

Mass Transfer Mechanisms - Reverse Osmosis Membrane

Membranes capable of retaining solutes whose molecular diameters are about 10^6 \AA or less, function as diffusional transport barriers (19). In these membranes, both solute and solvent migrate by molecular diffusion under concentration gradients which are established in the membrane by the applied pressure difference. In such cases, the driving force pressure for efficient separation must exceed the osmotic pressure of the solute in the solution. In 1885, Van't Hoff (16) showed that osmotic pressure π_A , in dilute solutions is related to the concentration of the solute, C_A , by the following relation:

$$\pi_A = \frac{R T C_A}{M}$$

where

R = Gas Constant ($0.08205 \text{ atm /g-mole}^\circ\text{K}$)

T = Absolute Temperature ($^\circ\text{K}$)

C_A = Concentration of Solute A (g/l)

M = Molecular Weight of Solute A

The osmotic pressure difference across the membrane, $\Delta\Pi$, is the difference between the osmotic pressure at the membrane surface, Π_w , and the osmotic pressure of the permeate, Π_p .

$$\Delta\Pi = \Pi_w - \Pi_p$$

The solvent and solute transport rates across the membrane can be approximated by the following relationships (2,19). For the solvent:

$$J_1 = \frac{\bar{P}_1}{t_m} (\Delta p - \Delta\Pi) = \frac{\bar{C}_1 \bar{D}_1 \bar{V}_1}{t_m R T} (\Delta p - \Delta\Pi) \quad (1)$$

where

J_1 = Solvent Flux ($\text{cm}^3/\text{cm}^2\text{-sec}$)

t_m = Membrane Thickness (cm)

\bar{P}_1 = Membrane Permeability Constant of Solvent ($\text{cm}^2/\text{sec-atm}$)

Δp = Hydrostatic Pressure Difference (atm)

$\Delta\Pi$ = Solute Osmotic Pressure Difference between Upstream and Downstream Solutions (atm)

\bar{C}_1 = Mean Concentration of Solvent in Membrane (cm^3/cm^3)

\bar{D}_1 = Diffusivity of Solvent in Membrane (cm^2/sec)

\bar{V}_1 = Partial Molar Volume of Water in Solution (cm^3/mole)

R = Gas Constant ($0.08205 \text{ atm-l/g-mole } ^\circ\text{K}$)

T = Absolute Temperature ($^\circ\text{K}$)

For the solute:

$$J_2 = \frac{\bar{P}_2}{t_m} (C_B - C_P) = \frac{K_2 \bar{D}_2}{t_m} (C_B - C_P) \quad (2)$$

Where

\bar{P}_2 = Membrane Permeability Constant of Solute
(cm²/sec atm)

J_2 = Solute Flux (g/cm²-sec)

K_2 = Solute Distribution Coefficient between Membrane and solution

D_2 = Solute Diffusivity in Membrane (cm²/sec)

C_B = Upstream Solute Concentration (g/cm³)

C_P = Downstream Solute Concentration (g/cm³)

However, mass conservation requires that

$$J_2 = J_1 C_P$$

Simultaneous solution of equation (1), (2), and (3) yields the following result:

$$1 - \left(\frac{C_P}{C_B}\right) = R = \frac{(\bar{P}_1/\bar{P}_2)(\Delta P - \Delta \pi)}{1 + (\bar{P}_1/\bar{P}_2)(\Delta P - \Delta \pi)} \quad (3)$$

The quantity R is the 'rejection coefficient' of the membrane. It is the fraction of the solute present in the upstream solution which is retained by the membrane.

The solvent flux is directly proportional to the effective pressure difference across the membrane. The rejection efficiency of the membrane increases asymptotically with increasing pressure difference, but will never meet the theoretical limit of unity as the applied pressure increases to infinity which is due to the coupling of solute and solvent flow. As a matter of fact, the pressure difference is increased as well as the solute

permeability coefficient which may have a compression effect on the membrane at higher pressure (2,19).

The Kimura-Sourirajan Analysis (20)

The analysis of transport phenomena is based on the generalized capillary flow model. It is applicable only for binary solution systems under isothermal condition and permeate collected at atmospheric pressure. The following equations can be applied to all level solute separation:

$$A = \frac{(PWP)}{M_B \times S \times 3600 \times P} \quad (4)$$

$$N_B = A(P - \pi(X_{A2}) + \pi(X_{A3})) \quad (5)$$

$$= \frac{D_{AM}}{k\delta} \left(\frac{1 - X_{A3}}{X_{A3}} \right) (C_2 X_{A2} - C_3 X_{A3}) \quad (6)$$

$$= kC_1(1 - X_{A3}) \ln \left(\frac{X_{A2} - X_{A3}}{X_{A1} - X_{A3}} \right) \quad (7)$$

Where

N_B = Solvent flux through membrane (g-mole/cm²-sec)

(PWP) = Pure water permeation rate (g/hr per given area of film surface)

M_B = Molecular weight of water

S = Area of membrane surface (cm²)

P = Operating pressure (atm)

A = Pure water permeability constant (g-mole H₂O/cm²-sec-atm)

$\pi(X_{A3})$ = Osmotic pressure of solution corresponding to mole fraction of solute X_A on the low pressure side of the membrane in the system (atm)

$\pi(X_{A2})$ = Osmotic pressure of solution corresponding to mole fraction of solution X_A on the high pressure side of the membrane in the system (atm)

$D_{AM}/K\delta$ = Solute transport parameter treated as a single quantity (cm/sec)

X_A = Mole of solute in Q'

Q' = Product rate (g/cm²sec)

c = Molar density of solution (g-mole/cm³)

k = Mass transfer coefficient on the high pressure side of the membrane (cm/sec)

Subscripts

1, 2, 3 refer to bulk solution (1) and concentrated boundary solution (2) on the high pressure side of the membrane and membrane-permeated product solution (3) on the low pressure side of the membrane respectively at any point (position or time) in the system.

The quantity A , the pure water permeability constant, is a measure of the overall porosity of the membrane under no concentration polarization effect. The solute transport parameter, $\frac{D_{AM}}{K\delta}$, is treated as a single quantity for the purpose of analysis. It plays the role of a mass transfer coefficient with respect to solute transport through the membrane.

If this set of equations applies to experimental data on pure water permeation rate, (PWP) membrane-permeated product rate (PR), and solute separation R , A , X_{A2} , $(\frac{D_{AB}}{K\delta})$, and K can be determined at any point in the R.O. system.

Mass Transfer Mechanisms - Ultrafiltration Membrane

Ultrafiltration membranes, those retaining particles larger than 10^5\AA , seem to function as molecular screens characterized by the pore size. Water and low-molecular weight solutes, such as salts and some surfactants, pass through the membrane and are removed as permeate. Suspended solids, emulsified oil and high-molecular weight species are rejected by the membrane

and are removed as concentrate (14,17). The simplified transport relations are: (19)

For the solvent:

$$J_1 = \frac{K_1 \Delta P}{\mu t} \quad (5)$$

where:

μ = the solvent viscosity

For the solute:

$$J_2 = C_P J_1 = \sigma_2 J_1 C_B \quad (6)$$

where:

σ_2 = dimensionless constant

$$(0 < \sigma < 1)$$

For rejection efficiency,

$$\sigma_2 = \frac{C_P}{C_B} = 1 - R \quad (7)$$

Since (σ_2) is determined solely by the solute molecular dimensions and the pore size distribution in the membrane, the membrane rejection efficiency is independent of applied pressure even though transport is pressure driven. The osmotic pressure of macromolecular solution would appear to be insignificant based on molecular weight considerations (12).

Concentration Polarization

When a solution is ultrafiltered through a high permeability membrane which is completely or partially retentive for one or more of the solutes present, the observed flux rate at any applied pressure is invariably lower, and often far lower than the value

measured with pure solvent at the corresponding pressure. The flux reduction is not attributable to 'plugging' of the ultrafiltration membrane, but rather to the accumulation on the upstream surface of the membrane of a layer of highly concentrated solution of retained solute convectively transported to the membrane by the flow of solvent through the membrane. This phenomenon is called 'concentration polarization' (18).

The influence of polarization upon membrane performance characteristics is always adverse and frequently severe. During water demineralization by reverse osmosis, the high solute osmotic pressure in the boundary layer will reduce further the effective pressure, and as a matter of fact, reducing the solvent flux. For ultrafiltration processes, the solution contains a high-molecular-weight solute or colloid. The ultrafiltration rate decreases which is due to solute accumulation at the membrane surface producing a hydraulic flow resistance finite layer. It is not osmotic pressure effects as in reverse osmosis processes because the high concentration gradient away from the membrane surface is required to diffuse the solute back to the bulk solution. But, high-molecular-weight solutes which have very low diffusion coefficient tend to form a gel layer on the membrane surface (Figure 3). The hydraulic resistance of the gel layer is often greater than that of the membrane and becomes the controlling factor for membrane flux. Figure 4 shows the concentration profile near the membrane surface (8,12).

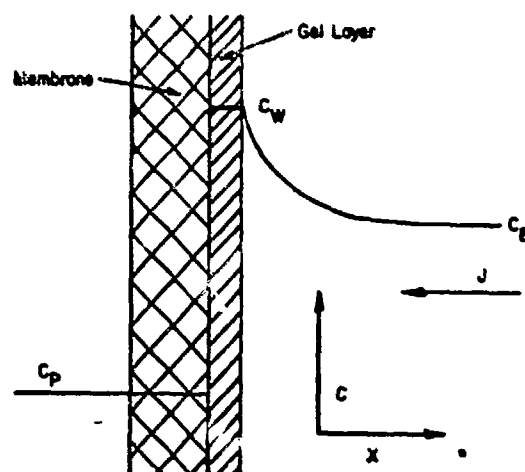


Figure 3. Concentration Polarization Schematic

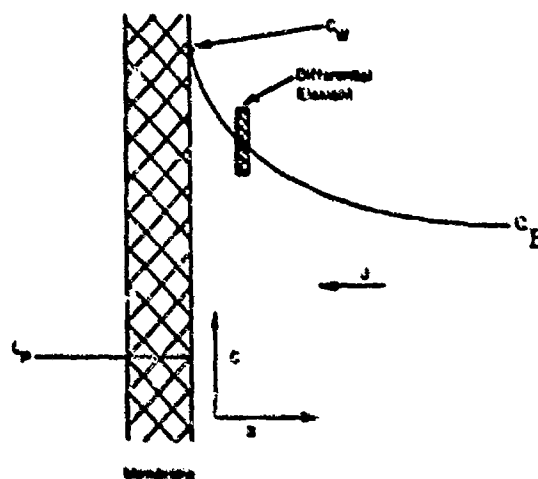


Figure 4. Concentration Profile near the Membrane Surface at Steady-State Conditions

A material balance shows,

$$J_1 C = D \frac{dc}{dx} + J_1 C_P \quad (8)$$

$$\frac{J_1}{D} \int_0^d dx = \int_{C_S}^{C_W} \frac{dC}{C - C_P}$$

$$J_1 = \frac{D}{d} \ln \left(\frac{C_W - C_P}{C_B - C_P} \right) \quad (9)$$

For high rejection membrane (12,13,18), where $C_P \ll C_W, C_B$, Equation (9) becomes

$$\frac{J_1 D}{d} = \ln \left(\frac{C_W}{C_B} \right) \quad (10)$$

$$M = \frac{C_W}{C_B} = \exp \left(\frac{J_1 D}{d} \right) \quad (11)$$

where

J_1 = Solution flux through the membrane ($\text{cm}^3/\text{cm}^2\text{-sec}$)

C_W = Solution concentration at the membrane surface (g/cm^3)

C_B = Upstream solute concentration (g/cm^3)

C_P = Downstream solute concentration (g/cm^3)

D = Solute diffusivity (cm^2/sec)

d = Concentration boundary-layer thickness (cm)

This relation indicates that polarization is particularly severe with high solvent permeability membranes and high molecular weight

solutes having a smaller value of diffusivity, D . The boundary layer thickness is uniquely determined by the dimensions of the membrane bounded channel and the flow regime (laminar or turbulent) (18).

For ultrafiltration, although the transport is pressure driven, the ultrafiltration flux of macromolecular solutions is independent of pressure. In general, increasing the driving pressure will observe the transient increase of the solvent flux. However, the transport of solute to the membrane surface by the permeation must still be balanced by the diffusion of accumulated solute at the membrane surface back into the bulk solution.

Indeed, increasing pressure does not intensify this back diffusion effect so that a transient rate of accumulation of solute at the membrane surface will occur. As a matter of fact, the permeation resistance of the gel layer has increased just to the extent to counterbalance the higher solution flux at a new steady state which is due to an increase in pressure.

II. MATERIALS

Chemical

Fire fighting agents used in military services are commonly referred to as Aqueous Film Forming Foam (AFFF). Currently three major AFFF products are available on the market, Ansul, 3M FC-206, and 3M FC-780. Dr. D. B. Chan of the U.S. Navy Civil Engineering Laboratory, Port Hueneme, California arranged for ten 18.93 liter (5 gallon) samples of each of the three AFFF stock solutions from the respective product manufacturers for this research study.

Type of Wastewaters

Fire fighting training exercises at military installation consume large quantities of water and fire fighting chemical agents. It results in intermittent discharges of waste streams containing high strength of potentially toxic pollutants. In membrane process studies, tap water or samples of direct discharge wastewater generated from fire fighting exercises were spiked with 3% to 6% of AFFF for evaluation.

Experimental Set-Up

Two types of pilot-scale experimental systems were employed in this study, ultrafiltration and reverse osmosis membrane processes. Experimental set-ups of these pilot-scale systems are briefly discussed in the following paragraphs.

For ultrafiltration, the membrane flux is governed by the feed rate in order to minimize the concentration polarization effect on the membrane surface. Batch operation (Figure 5) (15) has been employed in this study. This system requires a large processing tank. One disadvantage is that the agitating action of the return retentate in the bulk solution of AFFF wastewater creates foaming which causes undesirable loss of foams and feed. As a result, the ultrafiltration pilot-plant was modified based on the principle of continuous feed and bleed mode of operation (Figure 6) (15). However, the main disadvantage of this mode of operation is that the system has to be operated at the concentration level of the retentate stream which will reduce the permeate flux and intensify the concentration polarization effect on the membrane surface. Combining both operation modes, the foaming problem was suppressed and the disadvantage of the above modes of operation was minimized.

A schematic diagram of the system is shown in Figure 7. In this mode of operation, the majority of the feed is recirculated in a loop through the membranes. Approximately 2 to 5 times of the permeate flow rate of fresh feed is introduced into the loop. The make-up feed is introduced into the pumping loop for both the fluid that permeate through the membrane and the portion of liquid in the circulation loop that is bled back to the feed tank. This method reduces both power consumption and piping size. However, the ultrafiltration system must be located far from the feed tank. The economy provided by this system is that

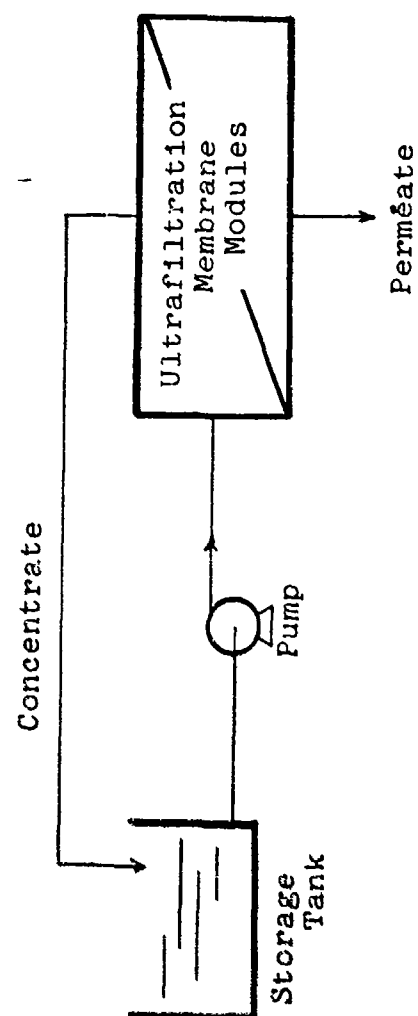


Figure 5. Batch Operation of an Ultrafiltration System

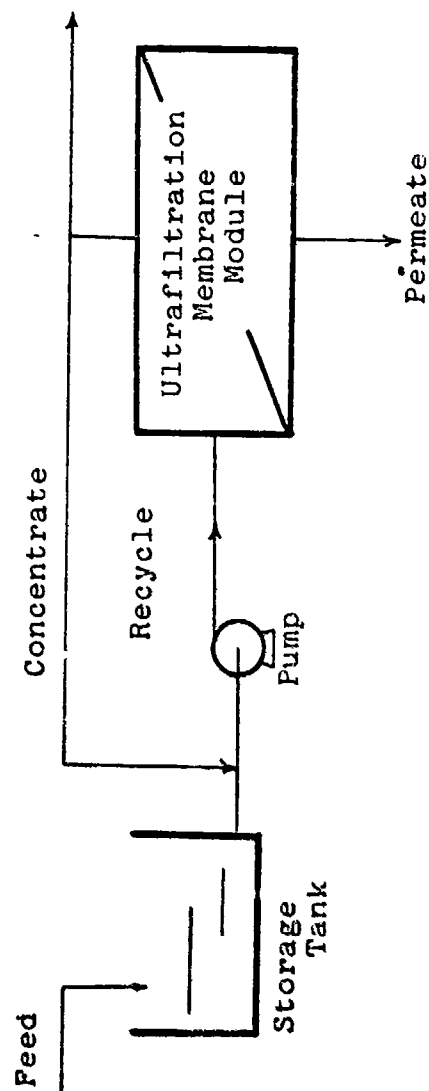


Figure 6. Continuous Feed and Bleed Operation of an Ultrafiltration System

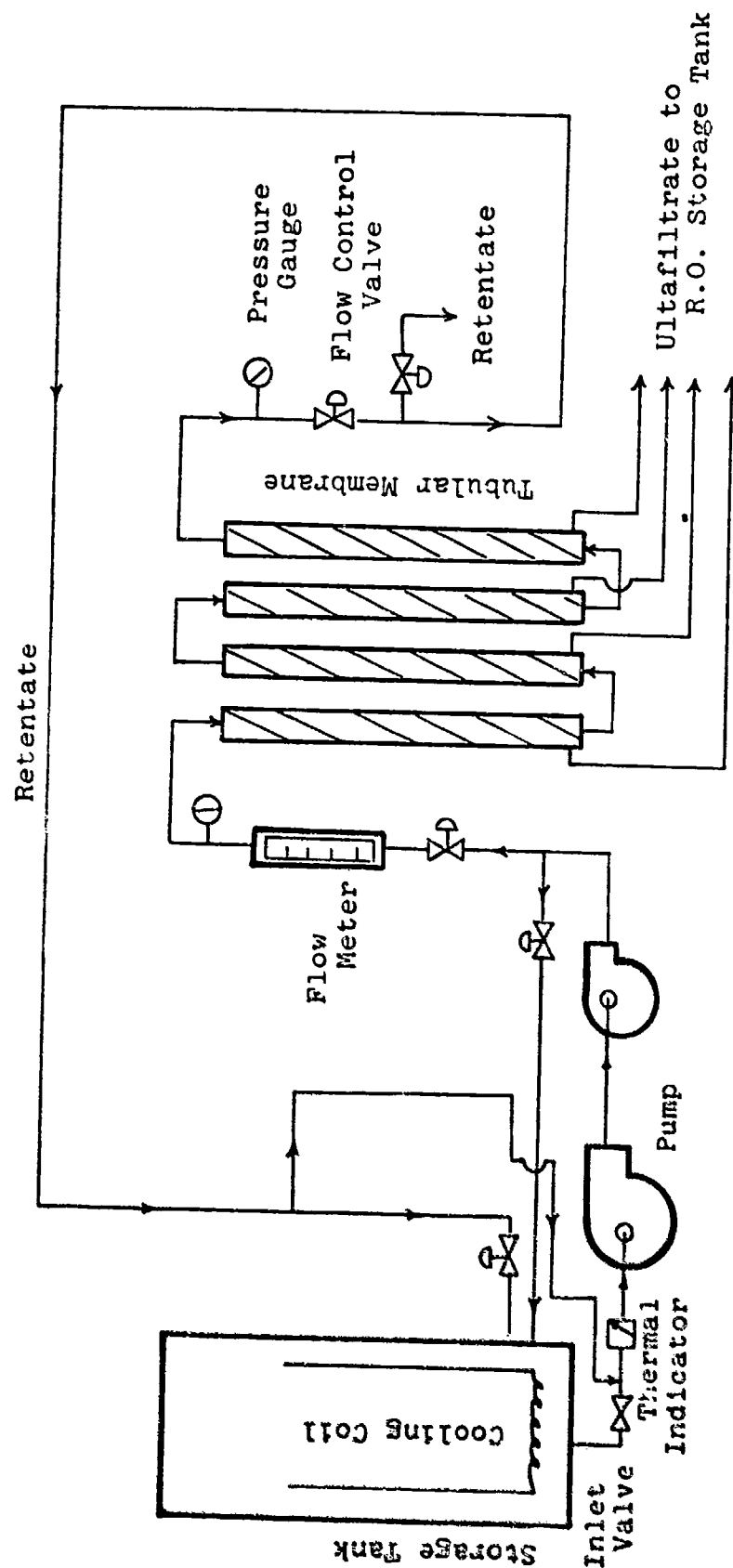


Figure 7. A Schematic Diagram of the Ultrafiltration Pilot-Plant

the feed does not drop to a zero pressure in the recirculation loop as in the original design. A finite pressure maintained in the loop significantly reduces pump size required to build up pressure for the ultrafiltration process.

Piping. The system was operated below 3.4 atm (50 psig). Plastics such as polyethylene (PE), polyvinyl chloride (PVC), and acrylonitrile-butadiene-styrene (ABS) were used because plastic piping provides the best mechanical properties for meeting the pressure and corrosion resistance requirements. Precautions were taken to protect the piping from vibration, water hammer and external abuse.

Feed Pump. The bulk solution was fed into the tubular membrane modules by connecting two TEEL centrifugal pumps in series (Model 1P702 and 1P701, Dayton Electric Mfg. Co., Chicago, IL), having 1 1/2 and 3/4 H.P. drive motors, respectively.

Membranes. For the membrane selection, Abcor's (HFD, HFF, HFK and HFJ, Wilmington, MA) 5 feet by 1 inch tubular membranes were tested. Two sets of Abcor HFD and HFF, HFK and HFJ tubular membranes were connected in series in the different phases of this study. Membrane flux is defined by cubic meter per square meter per day ($\text{m}^3/\text{m}^2/\text{day}$). A cut-away view of a tubular module is illustrated in Figure 8 (1) to demonstrate the specific features of the Abcor's tubular membrane module.

System and Equipment Design for Reverse Osmosis

In reverse osmosis, the existence of a pressure gradient drives permeation through a semi-permeable membrane, separating the feed stream into a concentrate and a dilute fraction. The desired product in this case study is the concentrate. The

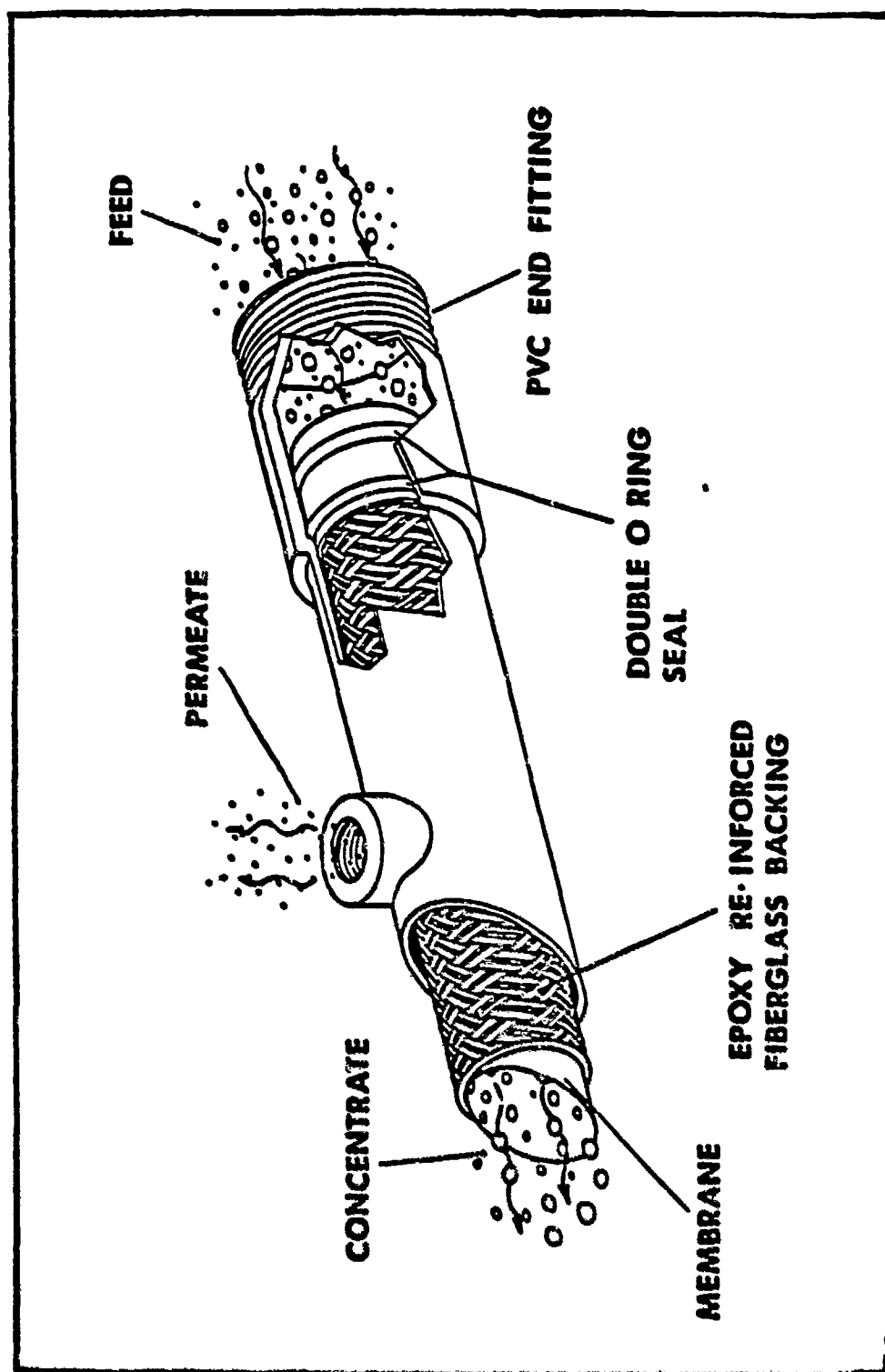


Figure 8. Cut-Away View of a Tubular Ultrafiltration Assembly (1)

major performance parameters of the membrane device are its product stream concentration which depends largely on the rejection characteristics of the semi-permeable membrane and the operating pressure. A single stage DuPont B-10 permeator was installed and is shown in Figure 9.

Piping. Type 316 stainless steel was chosen for the high-pressure piping system. Sufficient fresh water flushing is required to avoid corrosion due to stagnation during the period of pilot-plant shutdown.

Feed Pump. The bulk solution was fed into the Permasep permeator by means of a triplex positive displacement pump (Model No. 00500, Cat Pumps, Minneapolis, MN) driven by a 5 H.P. motor (Dayton Electric Mfg. Co., Chicago, IL).

Constant Pressure-Control Devices. A triplex positive displacement pump tends to minimize the possibility of system failure due to excessive pulsation. Additional hydraulic devices were installed (two 1-quart water service accumulators Model No. 30A-1/4WS Greer Hydraulics, Chatsworth, Calif.) downstream of the positive displacement pump in order to further damp out the hydraulic shock and significantly minimize vibrations in the system. Relief valves were installed to protect the pumping system from excess pressure build-up. The pressure regulator on the concentration stream is used to control the pressure of the system.

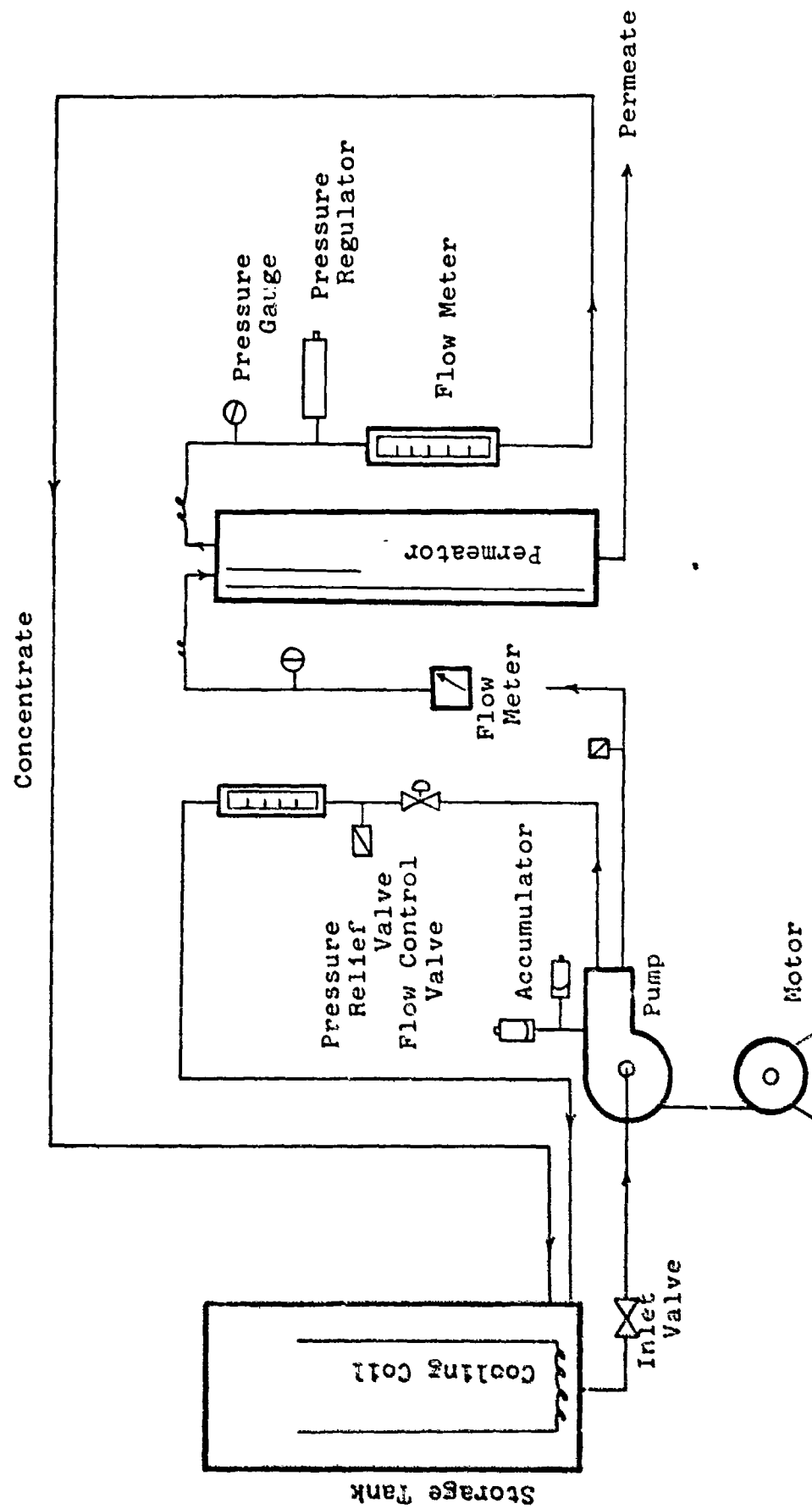


Figure 9. A Schematic Diagram of the Reverse Osmosis Pilot-Plant

Membrane. A full size 12.7 cm (5 in.) diameter by 1.22 m (4 ft) B-10 aramid Permasep permeator (Model No. 6440-015, DuPont Company, Wilmington, DE) was used for the reverse osmosis study. Membrane flux is defined by cubic meter per day per module (m^3pd). The Permasep permeator specifications are presented in Table 2 (9). A cut-away view of the Permasep permeator (Figure 10) gives the general idea how it functions (4,9).

Table 2 (9)

Permasep Permeator
 Model No. 6440-015
 5" Diameter B-10 Permeators
 Product Specifications

Membrane type	B-10 aramid
Membrane configuration	Hollow fiber
Shell dimensions	5-1/2" OD x 4-5/8" ID x 48-1/2" long (14.0 cm OD x 11.7 cm ID x 123.2 cm long)
Shell material	Filament-wound fiberglass epoxy
End plates and segmented rings	Fiberglass epoxy
Connections	Feed and product, 1/2" female, NPT Brine, 3/8" female, NPT Brine sample, 1/8" female, NPT
Permeator weight, filled with water	50 pounds (22.7 kg)
Operating position	Horizontal or vertical
Initial product water capacity ¹	1,500 min. — 1,649 max gpd (5.68-6.24 m ³ /day)
Salt passage	≤ 1.5% ¹
Rated operating pressure	800 psig (5515 kPa)
Temperature range	0°-35°C (32°-95°F)
pH range ² , continuous exposure	5-9
Minimum brine rate	3,200 gpd (12.1 m ³ /day)
Maximum brine rate	9,600 gpd (36.3 m ³ /day)

1 : Based on operation with a feed of 30,000 mg/l NaCl, 800 psig (5515 kPa), 25°C, and 30% conversion.

2 : For operation outside this range, consult "Permasep" Products.

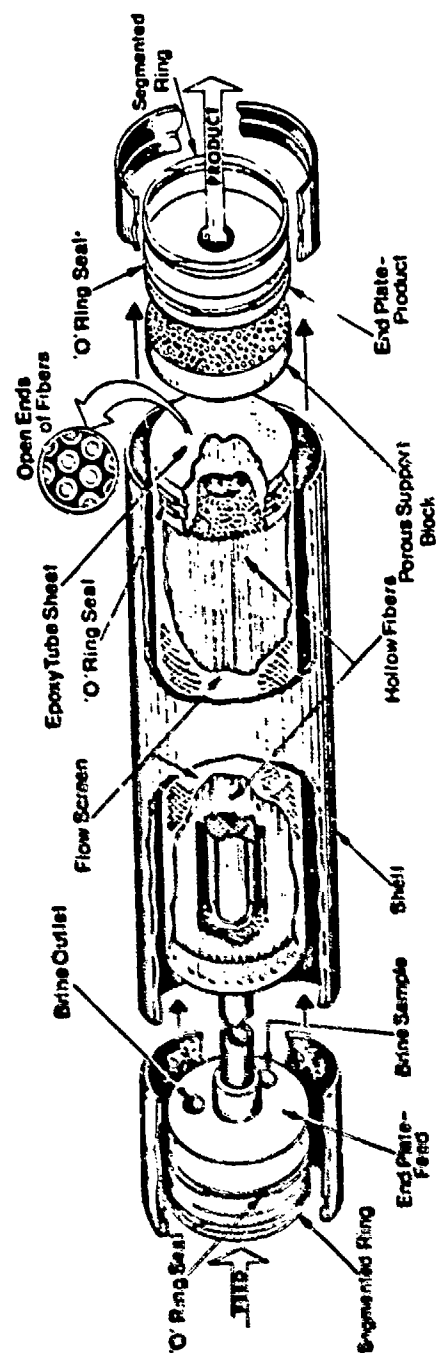


Figure 10. Cut-Away View of a Permapsep Permeator Reverse Osmosis Assembly (9)

III. EXPERIMENTAL PROCEDURE

Determination of the Optimum Operating Conditions for the Ultrafiltration and Reverse Osmosis Pilot-Scale Study Ultrafiltration

The membrane permeation rate (flux) and the rejection are a function of flow, pressure, temperature, and concentration.

Flow. An increase in feed flow rates through the tubular membrane system generally results in an increase in permeation rates. Because of the limitation of the pilot-scale set up, the flow rate was maintained between 60.58 to 68.15 liter per minute (16 to 18 gal/min) per pass of membrane modules.

Pressure. For the ultrafiltration membrane process, membrane fluxes of macromolecular solutions are found to be independent of pressure (8). In contrast, fluxes with pure water generally increase linearly with increasing pressure. The validity of this relation is based on Darcy's Law of laminar flow through porous media as shown in Figure 11 with tap water study. The Abcor HFJ ultrafiltration module is designed with a high flux membrane. The operating pressures range from 0.68 to 1.36 atm (10 to 20 psig) are believed to be the transition range with respect to the permeation rate. Because of the unawareness of this phenomenon, no experimental data have been obtained in this transition range. Membrane fluxes for most macromolecule solutions are significantly lower than that measured for pure water under the same operating pressure. The operating pressure is set by the desired system flow conditions which

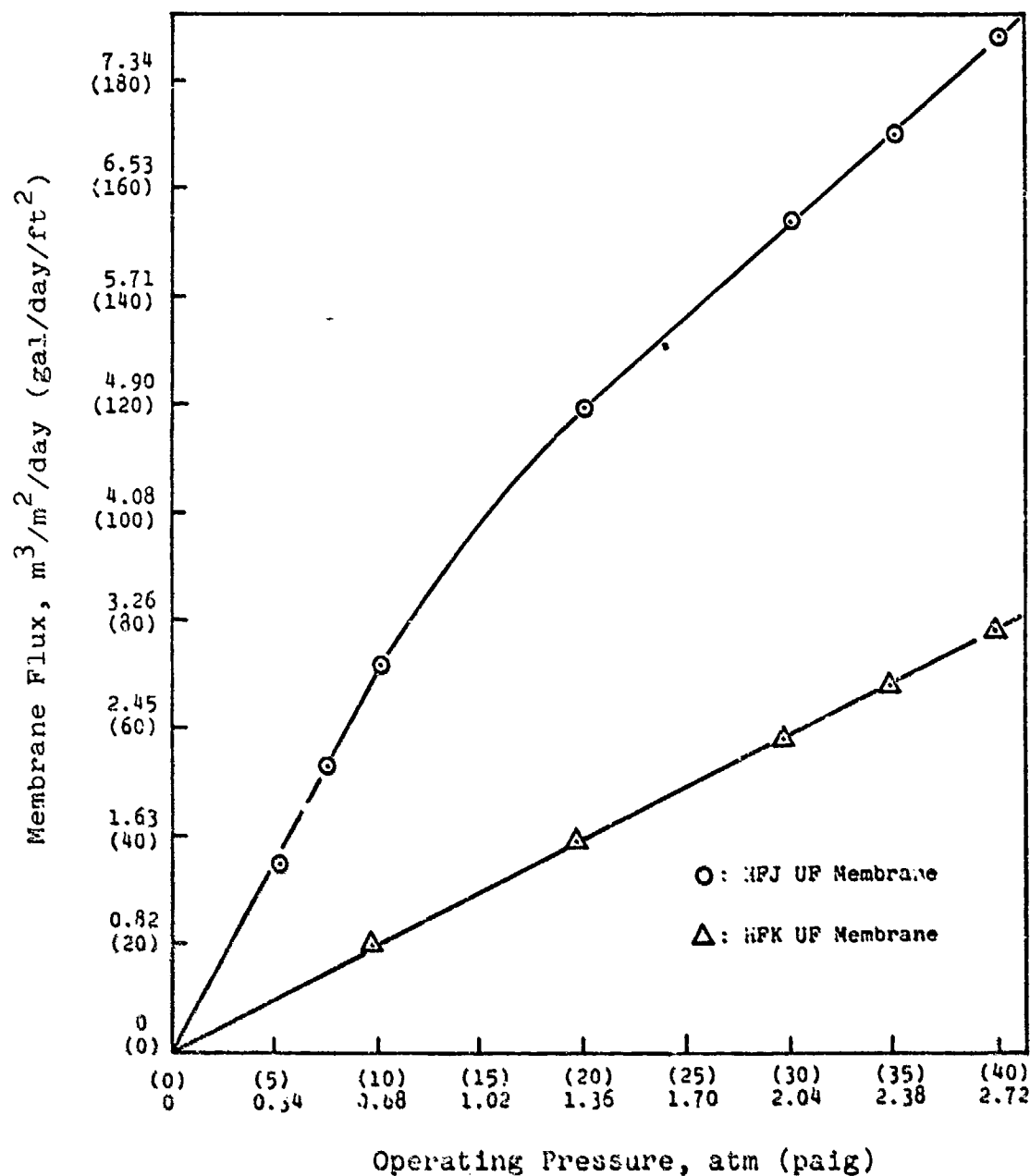


Figure 11. Abcor HFJ and HFK UF Membranes Pressure Effect Tap-Water Studies (Plotting Membrane Flux vs. Operating Pressure), at Constant Temperature, 25°C

are about 2.59 atm (38 psig) inlet pressure and 30 psig outlet pressure.

Concentration. Permeation rates decline with increasing concentration in the process feed stream. After a prolonged period of operation, cleaning is required to remove the buildups from the membrane surface to recover the module to its initial permeation flux level.

Temperature. Permeation rates increase with increasing temperature due to a decrease in fluid viscosity at high temperature. Figure 12 shows the tap-water flux vs. the reciprocal of water viscosity, operating temperature by the polymeric material used for membrane fabrication and the operating pressure. For the low pressure Abcor ultrafiltration membranes, the limits of operating temperature range from 5°C to 80°C. The operating temperature used for treating AFFF wastewater varied between 25°C to 50°C.

Reverse Osmosis

A full size DuPont B-10 Permasep permeator was employed in this study. The operating conditions are based on the manufacturer's specifications. However, due to an inadvertent error made in an earlier experiment by running the module at a high temperature (50°C), the module has suffered from heat damage. The permeator performance was recharacterized in this study. The membrane flux as indicated in Table 3 is drastically reduced. In reference to Table 3, the operating conditions to be employed in this reverse osmosis study are summarized as follows:

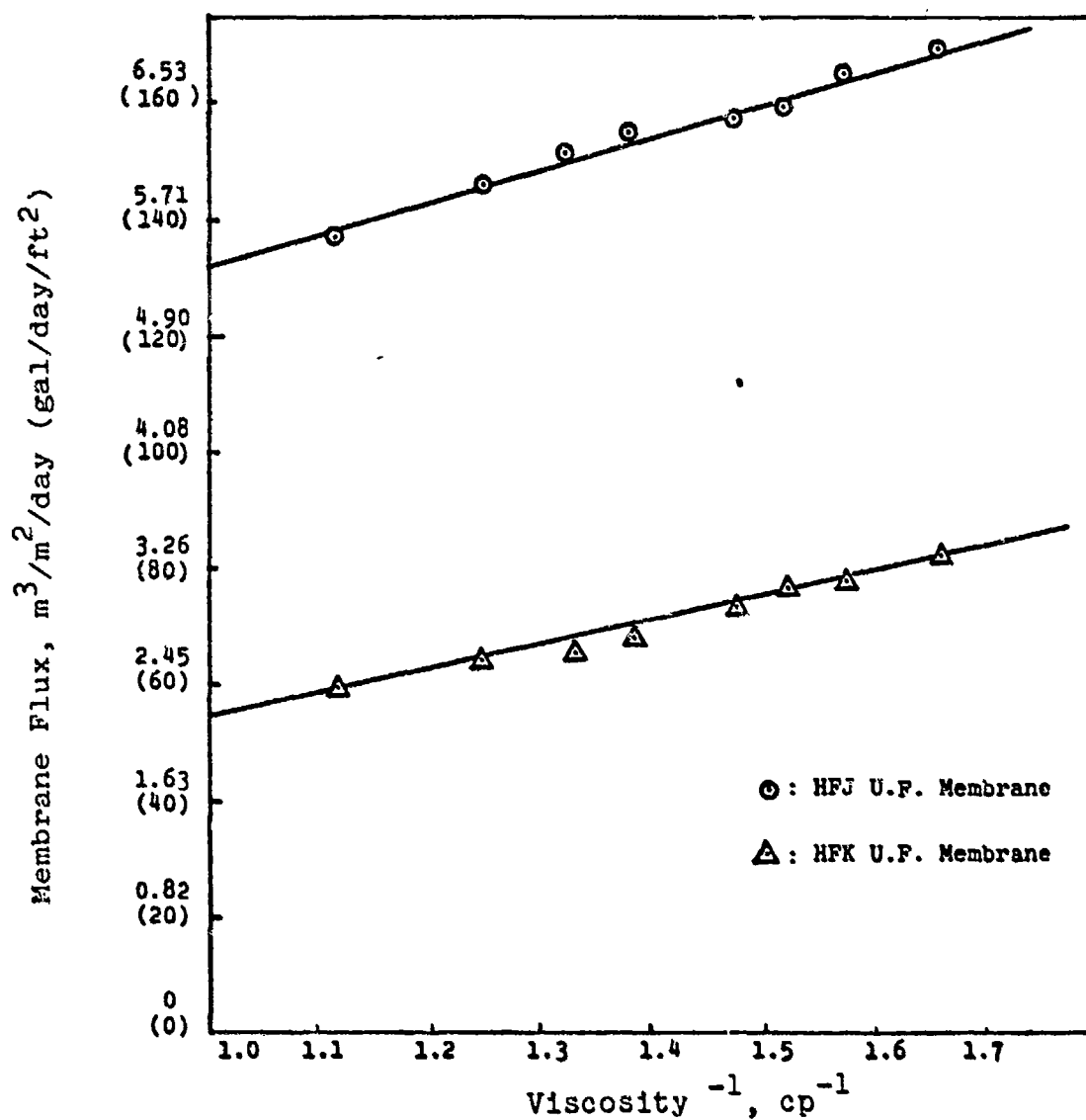


Figure 12. Abcor HFJ and HFK Ultrafiltration Membranes Temperature Effect Tap-Water Studies (Plotting Membrane Flux vs. Viscosity^{-1}), at Constant Operating Pressure, 2.04 atm (30 psig)

Table 3
DuPont B-10 RO Module Performance Study

Membrane : DuPont B-10 R.O. Module
 Sample : 0.23 cu. meter (60 gallons) 4,350 mg/l NaCl
 System : Batch
 Temperature: 25°C

1. At Constant Feed Rate, $0.91 \text{ m}^3/\text{hr}$. (240 gph)

Op. Pr. (atm)	Feed (mg/l)	Permeate (mg/l)	Flux (m^3/day)	Rejection (%)
13.61	4,350	87.5	2.13	97.99
27.21	4,250	52.5	4.85	98.76
40.82	4,250	47.75	7.58	98.88

2. At Constant Operated Pressure, 40, 82 atm (600 psig)

Feed Rate (m^3/hr)	Feed (mg/l)	Permeate (mg/l)	Flux (m^3/day)	Rejection (%)
0.49	4,100	85.0	7.14	97.93
0.91	4,250	44.0	7.58	98.96
1.34	4,350	39.0	7.58	99.10

3. At Constant Feed Rate, $0.91 \text{ m}^3/\text{hr}$. (240 gph) and Op. Pressure, 40.82 atm (600 psig)

Approx. Conc. Ratio	Feed (mg/l)	Permeate (mg/l)	Flux (m^3/day)	Rejection (%)
1.x	4,250	44.0	7.58	98.96
2.x	8,500	85.0	7.09	99.00
3.x	11,500	107.5	6.65	99.10
4.x	12,500	175.0	6.22	98.60
6.x	21,000	285.0	5.51	98.64

Temperature : 25°C
Flow : 15.14 μ /min (4 gal/min)
Operating Pressure: 40.82 atm (600 psig)

Feasibility Studies to Separate and Concentrate AFFF

Four different sets of membrane experiments were conducted. Abcor HFD and HFF ultrafiltration tubular membranes and DuPont B-10 permeator were used in the first and the second phase of the study; Abcor HFK and HFJ ultrafiltration tubular membranes and DuPont B-10 permeator were used in the third and final phase of the study. Membranes flux and rejection efficiencies were determined in order to characterize the membrane process performance.

Two types of experiments were conducted; namely, the differential test and the batch feed test. In the differential tests, the permeate from the membrane module is returned to the holding tank, thus maintaining a constant concentration of the feed in the tank. This test permitted the evaluation of the dependence of membrane performance in terms of both flux and rejection with time at a given feed concentration. In the batch feed test, the permeate is continuously discarded and the feed is allowed to concentrate to a predetermined level in the holding tank. This test procedure is used to determine the dependence of membrane performance on the feed concentration level.

In the first phase of the experiment, the test solution was a 6% solution (6 liters AFFF concentrate to 94 liters water) of each of the three AFFF concentrates i.e., Ansul, 3M FC-206,

and 3M FC-780 processed under the operating conditions as specified previously.

In the second phase of the study, two 208.23-liter (55-gallon) drums of direct discharge wastewater from fire fighting training exercises at military installations spiked with 3% Ansul and 3M FC-206 AFFF concentrates were used.

In the third phase of the membrane experiments, 6% solutions of both Ansul and 3M FC-206 concentrates were used.

The fourth phase of study was the same as the second phase experiment, the only difference was that a different wastewater spiked with 6% AFFF instead of 3% AFFF was used.

The reverse osmosis concentrates obtained from phases 2, 3, and 4 experiments were evaluated for their fire fighting capability at the Naval Research Laboratory (NRL) in Washington, D.C., under the supervision of NRL personnel.

Characterization of AFFF Concentrate and Wastewater Samples

Determination of the active constituents of the AFFF concentrates and the direct discharge was conducted for surfactant, glycols, and fluorocarbons (as fluoride). Gross parameters such as TOC, COD, total dissolved solids (conductivity), and foaming properties were also determined. In all the ultra-filtration and reverse osmosis experiments, the membranes were equilibrated to the experimental conditions for 30 minutes prior to any determinations being made or samples being collected. Procedures for the above analyses are presented below.

Surfactants

The surfactant test employed was the Methylene Blue Method for Methylene-Blue-Active Substances (MBAS) as given in Standard Methods for the Examination of Water and Wastewater (21). A Beckman Model 26 spectrophotometer (Fullerton, CA) was utilized for absorbance measurements. The stock linear alkyl sulphonate (LAS) solution used for calibration was an EPA standard LAS reference sample prepared by EMSL-Cincinnati, Ohio, U.S. EPA. Active LAS for the reference sample was 5.68% (Lot No. 7181 DATES878).

The foaming property of the samples was used to approximate the surfactant concentration. The foaming property was determined by the method commonly referred to as the shake test. This determination consists of placing 100 ml of sample in a 250 ml graduated cylinder with a secure fitting glass stopper. The sample is then shaken vigorously for 30 seconds and allowed to settle for five minutes, after each time, the foam volume in ml is recorded. The results of this method can be represented by the volume of the foam alone or calibrated against the same EPA LAS reference sample utilized in the MBAS method to determine equivalent mg/l of LAS.

Glycols

Chromatographs for the three AFFF stock solutions were determined using a Perkin-Elmer Sigma I Gas Chromatograph equipped with a FID (flame ionization detector). The column used was a 1.83 m long by 2 mm I.D. glass column packed with 10% Carbowax 20 M on 80/100 Chromasorb W. Chromatographic conditions were as follows:

Oven Temp. - Initial: 160°C for 6 min
Final: 200°C for 3 min
Rate: 10°C/min
Injection Temp.: 250°C
Injection Volume: 1 μ l
Detector Temp.: 300°C
Carrier Flow: N₂ at 30 ml/min
Air Flow: 240 ml/min
Hydrogen Flow: 30 ml/min
Chart Speed: - 0.5 cm/min

Fluorocarbons (as Fluoride)

The fluorocarbon concentration was estimated using a modification of the fluoride method developed by Chian (7). The method involves the substitution of fluorine ions for the chlorine ions on dichloro-phenyl-methyl silane under acidic conditions. The difluoro-phenyl-methyl silane is then determined by gas chromatography. The procedures for the method including sample preparation are given in detail below.

Sample Preparation. 5 ml of sample was mixed with 10 ml of 50% NaOH solution in a nickel crucible and heated over a Bunsen burner until the volume of solution becomes constant (approx. 2-3 ml). The sample was cooled and 10 ml of distilled water was added to dissolve the fused NaOH. The solution was brought to boil. Cool and add 10 ml of distilled water. Mix well, measure, and record volume.

Extraction with Dichloro-phenyl-methyl silane. Transfer 5 ml of sample digested as described above to a 30-ml separatory funnel. Dilute with 10 ml of distilled water and acidify with 10 ml reagent grade HCl (concentrated). Allow to cool. Add 1 ml of reagent prepared as described below, shake sample vigorously for 2 1/2 minutes and allow to settle for 30 minutes. Separate the lower solvent layer and analyze for difluoro-phenyl-methyl silane by injection of 1 microliter of the solvent extract on the GC column.

Reagent Preparation. The reagent employed in this method is prepared by dissolving 200 μ l of dichloro-phenyl-methyl silane in 100 ml methylene chloride.

Chromatographic Conditions - Perkin-Elmer Model Sigma I.

Column:	1.83 m by 2 mm i.d. glass column
Column Packing:	20% DC-200/100 on GCQ 100/120
Oven Temp. - Initial:	75°C for 10 min
Final:	120°C for 5 min
Rate:	5°C/min
Injection Temp.:	150°C
Detector Temp.:	300°C
Carrier Flow:	N ₂ at 32 ml/min
Air Flow:	300 ml/min
Hydrogen Flow:	30 ml/min
Chart Speed:	0.5 cm/min

Standard Curve. A standard solution containing 1 mg/ml of F^- was prepared, and dilutions of this solution were made. A standard curve was determined by treating these solutions containing known amounts of fluoride as described above.

Gross Parameters

COD. Chemical Oxygen Demand determinations were performed in accordance with Section 508 - Oxygen Demand (Chemical) of Standard Methods for the Examination of Water and Wastewater (21).

TOC. Total Organic Carbon determinations were performed in accordance with Section 505 - Organic Carbon (Total), Combustion - Infrared Method of Standard Methods for the Examination of Water and Wastewater (21). A Beckman 915 TOC Analyzer with a Model 865 Infrared Analyzer (Fullerton, CA) was utilized for the determinations.

Dissolved Solids. Dissolved Solids were determined using a Myron L Deluxe DS Meter (Model 532T1, Myron L Company, Encinitas, CA).

IV. RESULTS AND DISCUSSION

Characterization of AFFF Concentrate

The results of the AFFF characterization studies are summarized in Table 4. TOC analysis gave values of 117,000 mg/l, 110,000 mg/l, and 119,000 mg/l for 3M FC-206, 3M FC-780 and Ansul, respectively.

Surfactant analysis using the Methylene Blue Method (MBAS), Section 512A, Standard Methods (21) has its limitation as an indicator for the quantity of surfactant present. The AFFF concentrates are known to contain both nonionic and ionic surfactants but the Methylene Blue Method measures the concentration of anionic detergents only. The statistical results indicate that the MBAS method gives no significant information in determining surfactant concentrates containing AFFF constituents.

The results of the surfactant experiment obtained by the simple shake test seem to provide a reasonable approximation of surfactant concentration in AFFF, i.e., with diluted samples. The method gives comparative results between samples where same condition (dilution) must be maintained between each run, and the results are meaningful only for low concentrations of AFFF, i.e., with diluted samples. The results are then recorded as volume of foam or calibrated against the same EPA LAS standard used for MBAS to determine the amount in milligram per liter of LAS. The results of shake test give values of 110, 85 and 130 ml of foam under 1:500 dilution for 3M FC-206,

Table 4

Analysis of AFFF Concentrates

Parameter	3M FC-206	3M FC-780	Ansul
TOC, mg/l	117,000	110,000	119,000
Foam, ml (1:500)	110	85	130
TDS, mg/l	6,000	8,200	6,000

3M FC-780, and Ansul, respectively. High surfactants value for Ansul, at the same time, confirms the high value of TOC obtained with Ansul.

Because of the lack of knowledge of the specific glycols employed in the AFFF concentrates, GC/MS analysis of these compounds were conducted by Chang and Cooper (6). The results of this analysis, as reported by Chian (7), confirmed the presence of diethylene glycol mono-butyl ether in 3M FC-206, but failed to identify the specific compounds presented in Ansul. No attempt was made in this research to identify the specific glycols present in the AFFF concentrates. Since glycol can be determined by GC more specifically and more accurately than MBAS for surfactants and shake test, it may be used more confidently in estimating the concentration of glycols in fire fighting solution.

Fluoride analysis, where Standard Methods (21) or modified procedures described earlier were employed, did not give the expected results. Statistical analysis of the results indicate that the poor reproducibility of the above method was due to matrix effect or interferences, such as the presence of high concentrations of chloride ion used in neutralizing the fused NaOH solution and the use of H_2SO_4 as a neutralizing agent. The latter caused loss of sample in the direct fusion or ashing step, etc., thus making the fluoride results for AFFF unreliable.

Characterization of Direct Discharge Fire Fighting
Training Exercise Wastewaters

The results of characterization of the wastewaters from two different locations are summarized in Table 5 and 6. Concentration values were expected to be lower than the daily training in the fire fighting training school which also depend on the type of fire fighting training being employed and the frequency being exercised. The training exercise is located in a shallow pond. The wastewater generated from the training exercise collection from Warner-Robbins Air Force Base has been mixed with pond water. However, both wastes have a strong odor of jet fuel. Since a 6% solution of AFFF concentrate is being used in fire fighting exercises, during the membrane treatment experiments, the wastewaters were spiked with virgin AFFF to bring the AFFF concentrate in the wastewater up to 3% or 6% AFFF solution level for the purpose of study in the recovery of AFFF ingredients. However, it is not known how much of glycol, surfactants and fluorocarbons may have burned off during the fire fightings exercises.

Membrane Processes

The purpose of these experiments was to study the potential of using membrane processes to recover the active ingredients in the AFFF concentrate for reuse and to investigate the possibility of improving the membrane scheme by selection of membrane type and characteristics. Two terms, volumetric concentration ratio (VCR) and product water recovery (PWR),

Table 5

Characterization of Fire Fighting Trainging
Exercise Wastewater

Location : San Diego

Sample : Two - 0.21 cu. meter (55 gallons) wastewater from
a medium sized fire fighting exercise using 1.51
cu. meter (400 gallons) JP-4 jet fuel

<u>Parameter</u>	<u>Average value</u>
COD, mg/l	800
TOC, mg/l	338
Glycol, % of Conc.	0.0007
Surfactants (mg/l LAS)	30

Table 6

Characterization of Fire Fighting Training
Exercise Wastewater

Location : Warner-Robbins Air Force Base'
Sample : Two - 0.21 cu. meters(55 gallons) wastewater from
a medium sized fire fighting exercise using 2.27
cu. meters (600 gallons) JP-4 jet fuel
Agent : 6% 3M AFFF
Date : July 3, 1980

Parameter	1st drum	2nd drum
TOC, mg/l	450	540
TDS, mg/l	192.5	195
Glycol, % of Conc.	0.035	0.065
Surfactants (foam, ml)	30.0	35.0

were used throughout the study, their relationships are presented in Table 7. The first and the second phases of the experiments were mainly a feasibility study, while the third and the fourth phase of the experiments were directed toward evaluating the performance of membrane processes for recovery of active ingredients from fire fighting wastewaters.

First Phase Experiment with 6% AFFF (Tap-Water) Study

In this initial phase of the membrane studies, 6% solution of each of the three AFFF concentrates was prepared and run through the ultrafiltration (UF) and reverse osmosis (RO) systems using a 0.11 cu. meter (30 gallon) holding tank, operated in the batch mode. Technical problems occurred because of the high degree of agitation inherent in the laboratory scale UF set up, creating foaming problems. Ideally, the UF process should retain as little as possible of the AFFF active constituents, as represented by the various parameters monitored in these experiments. For the overall permeate collected from UF under the batch feed test, it can be seen from Table 8 that the ideal result of zero rejection of AFFF ingredients by UF membranes are not attained. By comparison, both Abcor HFD and HFF UF membranes were favorable for treating 3M FC-206 or 3M FC-780 AFFF over Ansul. Membrane fluxes were approximately $2.04 \text{ m}^3/\text{m}^2/\text{day}$ (50 gal/ft²/day) for a 6% AFFF solution at 25 C. This flux declined with increasing volume reduction. At 66.67% product water recovery, the measurement decreased to approximately $1.43 \text{ m}^3/\text{m}^2/\text{day}$ (35 gal/ft²/day). As a matter of fact, this

Table 7

Relationships between VCR, VRR, and PWR

VCR*	VRR**	PWR, %***
1x	1x	0
2x	1/2x	50.00
3x	2/3x	66.67
4x	3/4x	75.00
5x	4/5x	80.00
6x	5/6x	83.30
10x	9/10x	90.00

* Volumetric Concentration Ratio

** Volume Reduction Ratio

*** Product Water Recovery

Table 8

Overall Rejection of HFD and HFF
Ultrafiltration Membranes Study with
6% AFFF Tap-Water Solution

AFFF Sample	Overall Rejection, (%)				
	Glycol	TOC	Surfactants	TDS	PWR*, %
Ansul	12.16	14.6	41.00	N.D.	66.67
3M FC-206	6.56	7.0	9.00	13.24	66.67
3M FC-780	11.90	11.0	17.33	13.00	80.00

* PWR : Product Water Recovery
N.D. : Not Determined

observation indicates that UF membranes have rejection of AFFF ingredients.

The results of differential test studies are summarized in Tables 9, 10 and 11. Comparatively, Ansul has shown higher rejections with samples at all concentration levels, probably because of the foaming. It may also be that the HFD and HFF membranes are not the choice membrane of Ansul AFFF treatment.

The permeate from the UF experiment was saved and used as the feed solution for the RO process. Table 12 shows over 99% of the active ingredients, such as TOC, glycols, surfactants, etc., can be retained by the RO membrane processes. Because of the high removal efficiencies of surfactants, fluorocarbons are also expected to be rejected by RO at high levels.

Second Phase Experiments with 3% Spiked AFFF Wastewaters Study

Two 0.21 cu. meter (55-gallon) samples from the direct discharge of an actual fire fighting exercise were obtained from San Diego, CA; one spiked with 3% Ansul, and the other spiked with 3% 3M FC-206. These samples were then treated in the UF-RO system as described previously for the tap-water experiments. Results of these wastewater experiments are summarized in Tables 13 and 14.

By comparison of feed samples and permeate samples, it is evident that the majority of the AFFF ingredients indeed pass the UF membrane, except that the surfactants have shown higher rejection, which may be again due to the excessive foaming in the feed tank.

Table 9
Results of Membrane Study with 6% Ansul Solution
with HFD and HFF Ultrafiltration Membranes (@ 25°C run)

HFD-Ultrafiltration Membranes									
Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection	
	Glycol (%)	TOC (mg/l)	COD (mg/l)	Surfactants* (mg/l LAS)	Glycol (%)	TOC (mg/l)	COD (mg/l)	Surfactants (mg/l LAS)	Surfactants (%)
1. X	5.1	5,900	24,445	3,000	5.30	4,916	21,775	1,500	--
3. X	5.6	7,300	28,555	4,700	N.D.	N.D.	N.D.	N.D.	N.D.
HFF-Ultrafiltration Membranes									
1. X	5.10	5,900	24,445	3,000	5.35	4,916	22,000	1,500	--
3. X	5.60	7,300	28,555	4,700	5.45	5,412	21,775	2,000	2.7
									23.7
									57

-- No Rejection

N.D. - Not Determined

* Determined by Shake Test

Table 10

Results of Membrane Study with 6% 3M FC-206 Solution
with HFD and HFF Ultrafiltration Membranes (@ 25°C run)

HFD-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples			Permeate Samples			Local Rejection		
	Glycol (%)	TOC (mg/l)	TDS Surfactants [*] (mg/l) (LAS)	Glycol (%)	TOC (mg/l)	TDS Surfactants (mg/l) (LAS)	Glycol (%)	TOC (%)	TDS Surfactants (%)
1. X	6.10	6,750	340	3,200	5.57	6,400	205	3,000	8.7 5.2 40 6
3. X	5.85	8,150	600	5,300	6.30	6,800	390	3,000	-- 16.6 35.0 44
<u>HFF-Ultrafiltration Membranes</u>									
1. X	6.10	6,750	340	3,200	5.62	6,150	200	3,000	7.9 8.9 40 6
3. X	5.85	8,150	600	5,300	5.90	N.D.	370	2950	-- N.D. 38.5 44

-- No Rejection

N.D. - Not Determined

* Determined by Shake Test

Table 11

Results of Membrane Study with 6% 3M FC-780 Solution
with HFD and HFF Ultrafiltration Membranes (@ 25°C run)

HFD-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples				*	Permeate Samples				Local Rejection			
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (mg/l LAS)		Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (mg/l LAS)	Glycol (%)	TOC (%)	TDS (%)	Surfactants (%)
1. X	6.30	7,250	385	3,750		6.30	6,650	245	3,100	--	8.3	36.4	17.
5. X	6.30	7,600	510	4,100		6.25	6,600	335	3,100	0.8	13.2	34.3	24.
HFF-Ultrafiltration Membranes													
1. X	6.30	7,250	385	3,750		N.D.	6,300	235	3,000	N.D.	13.1	39.0	20.
5. X	6.30	7,600	510	4,100		6.20	6,600	340	2,800	1.6	13.2	33.3	31.

-- No Rejection

N.D. - Not Determined

* Determined by Shake Test

Table 12

Results of Du Pont Reverse Osmosis B-10 Module Study
with Various 6% AFFF Solution from Ultrafiltration Permeate

6% Ansul

Approx. Conc.	Feed Samples				Permeate Samples				Local Rejection			
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants* (mg/l LAS)	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (mg/l LAS)	Glycol (%)	TOC (%)	TDS (%)	Surfactants (%)
1. X	4.48	4,646	N.D.	1,400	0.044	32.5	N.D.	11	99.0	99.3	N.D.	99.
2. X	8.80	8,685	N.D.	2,500	0.053	78.	N.D.	23	99.4	99.1	N.D.	99.
<u>6% 3M-FC 780</u>												
1. X	5.55	N.D.	335	2,250	0.065	N.D.	7.5	12.5	98.8	N.D.	97.8	99.
4.5X	23.0	22,000	1,300	4,000	0.365	N.D.	9.0	10.	98.4	N.D.	99.3	99.
<u>6% 3M-FC 206</u>												
1. X	5.70	6,700	295	3,200	0.056	73.	4.	31.5	99.0	98.9	98.6	99.
5.2X	29.72	36,000	1,200	6,100	0.476	585	10.	45.	98.4	99.3	99.2	99.

N.D. - Not Determined

* Determined by Shake Test

Table 13

Results of HFD and HFF Ultrafiltration Membranes Study
with 3% Ansul Spiked Fire Fighting Training Exercises
Wastewater from San Diego (@ 25°C run)

<u>HFD-Ultrafiltration Membranes</u>												
Approx. Conc. Ratio	<u>Feed Samples</u>			<u>Permeate Samples</u>					<u>Local Rejection</u>			
	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l LAS)	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l LAS)	Glycol (%)	TOC (%)	TDS (%)	Surfactants (%)	Surfactants* (%)	
1.x	2.5	3,200	1,275	2,300	2.45	N.D.	1,150	1,300	2.0	N.D.	9.8	43.
5.x	3.1	4,625	1,400	N.D.	2.9	3,825	1,350	1,700	4.0	17.2	9.8	43.
<u>HFF-Ultrafiltration Membranes</u>												
1.x	2.5	3,200	1,275	2,300	2.4	2,650	1,300	1,300	6.4	17.3	3.6	N.D.
5.x	3.1	4,625	1,400	N.D.	2.8	N.D.	1,600	1,600	9.7	N.D.	7.1	N.D.

N.D. - Not Determined

* Determined by Shake Test

Table 14

Results of HFD and HFF Ultrafiltration Membranes Study
with 3% 3M FC-206 Spiked Fire Fighting Training Exercises
Wastewater from San Diego (@ 25°C run)

HFD-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples			Permeate Samples			Local Rejection					
	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l LAS)	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l LAS)	Glycol (%)	TOC (%)	TDS Surfactants* (%)			
1.x	2.8	3,925	1,325	2,500	2.7	3,425	1,200	1,500	3.6	12.7	9.4	40
5.x	3.05	5,125	1,550	3,700	2.85	3,975	1,410	2,500	6.6	22.4	9.0	44
HFF-Ultrafiltration Membranes												
1.x	2.8	3,925	1,325	2,500	2.68	3,425	1,200	1,400	4.3	12.7	9.4	32
5.x	3.05	5,125	1,550	3,700	3.0	3,975	1,410	N.D.	1.6	22.4	9.0	N.D.

N.D. - Not Determined

* Determined by Shake Test

The greatest difference between the UF experiments with wastewater and the tap-water experiments is the significantly lower membrane flux. This reduced flux was not unexpected, however, as the wastewater contained many materials capable of fouling the UF membrane. For the wastewater spiked with 3% Ansol, the initial flux measured was approximately $1.43 \text{ m}^3/\text{m}^2/\text{day}$ ($35 \text{ gal}/\text{ft}^2/\text{day}$) at 25°C , as compared to the value of $2.04 \text{ m}^3/\text{m}^2/\text{day}$ ($50 \text{ gal}/\text{ft}^2/\text{day}$) determined for a 6% AFFF feed solution in tap-water study.

Excellent rejection of AFFF active ingredients was obtained with the RO membrane (Table 15). The results of these experiments were encouraging which led to the extensive studies in the third and fourth phases. Economic analysis of these membrane processes will then follow.

Third Phase Experiment with 6% AFFF (Tap-Water) Study

In this phase study, the pilot-plant for ultrafiltration studies was modified based on the principle of the continuous feed and bleed mode of operation. A 0.23 cu. meter (60-gallon) feed reservoir was employed in these studies in place of the 0.11 cu. meter (30-gallon) reservoir used previously. The foaming problem was suppressed successfully with this modified system. Because of the recirculation, the system was operated at the concentration level of the returned concentrate which would reduce the membrane flux. However, the heating of the recirculation loop by mechanical force actually reduced the viscosity and thus resulted in an increased membrane flux. In this case,

Table 15

Results of Du Pont Reverse Osmosis B-10 Module Study
 with Various 3% AFFF Spikes Fire Fighting Training Exercises
 Wastewater Solution from Ultrafiltration Permeate

3% Ansul Ultrafiltration Permeate

Approx. Conc. Ratio	Feed Samples				Permeate Samples				Local Rejection			
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants* (mg/l LAS)	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants* (mg/l LASO)	Glycol (%)	TOC (%)	TDS (%)	Surfactants* (%)
1.x	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
2.x	5.41	6,265	2,400	1,650	0.019	20	51	17	99.6	99.7	97.9	99.
3.75x	9.75	10,660	4,100	3,400	0.093	60	110	12	99.0	99.4	97.3	99.6
<u>3% 3M-FC 206 Ultrafiltration Permeate</u>												
1.x	2.48	3,655	1,150	1,800	0.038	188.5	18	18	98.5	94.8	97.3	99
4.x	9.60	12,088	4,200	3,750	0.142	204	120	16	98.5	98.3	97.1	99.6

N.D. - Not Determined

* Determined by Shake Test

operating at the RO retentate concentration level became an advantage. It saved energy required to heat the feed solution and increased the solute transport process from bulk to permeate solution.

At this point, local rejection evaluated from differential test was not an important parameter because of the higher concentration in the feed compared to that in the feed tank when only small rejection occurred initially. In order to evaluate the results of differential tests, the concentration of the constituents in the permeate at different volumetric ratios should be compared to the concentration of the constituents in the feed at the initial volume. An adjustable valve was installed to allow a small amount of concentrate return to the feed tank to minimize the concentration polarization effect on the membrane surface. The Abcor HFJ and HFK UF membranes were also evaluated in the same manner.

The importance of the operating temperature in the UF process can be observed in Figure 13. The flux at 50°C is almost double of that at 25°C for HFJ and HFK membranes. The membrane fluxes are very high which could render the process economically feasible. The difference in fluxes is caused by different operating temperatures which can be attributed to the reduction in viscosity at higher temperature. By comparing Figures 13 and 14 at 25°C, it is seen that a high flux is obtained with the 3M FC-206 using both HFJ and HFK membranes. This indicates that the membrane performance is depending upon the physical and chemical properties of the constituents of the

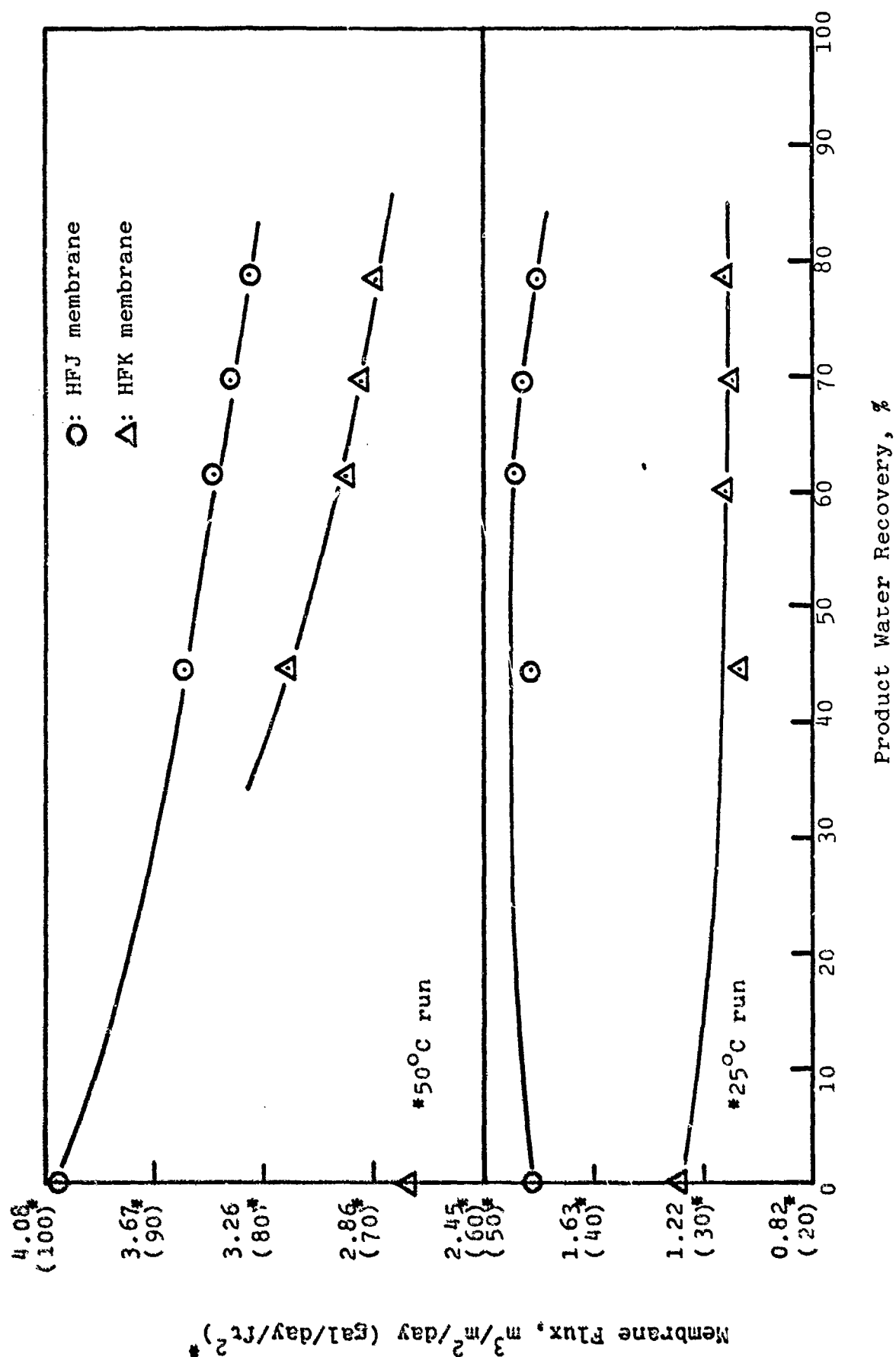


Figure 13. Effect of Temperature on Ultrafiltration Membrane Flux
(5% Ansul Solution with Tap-Water)

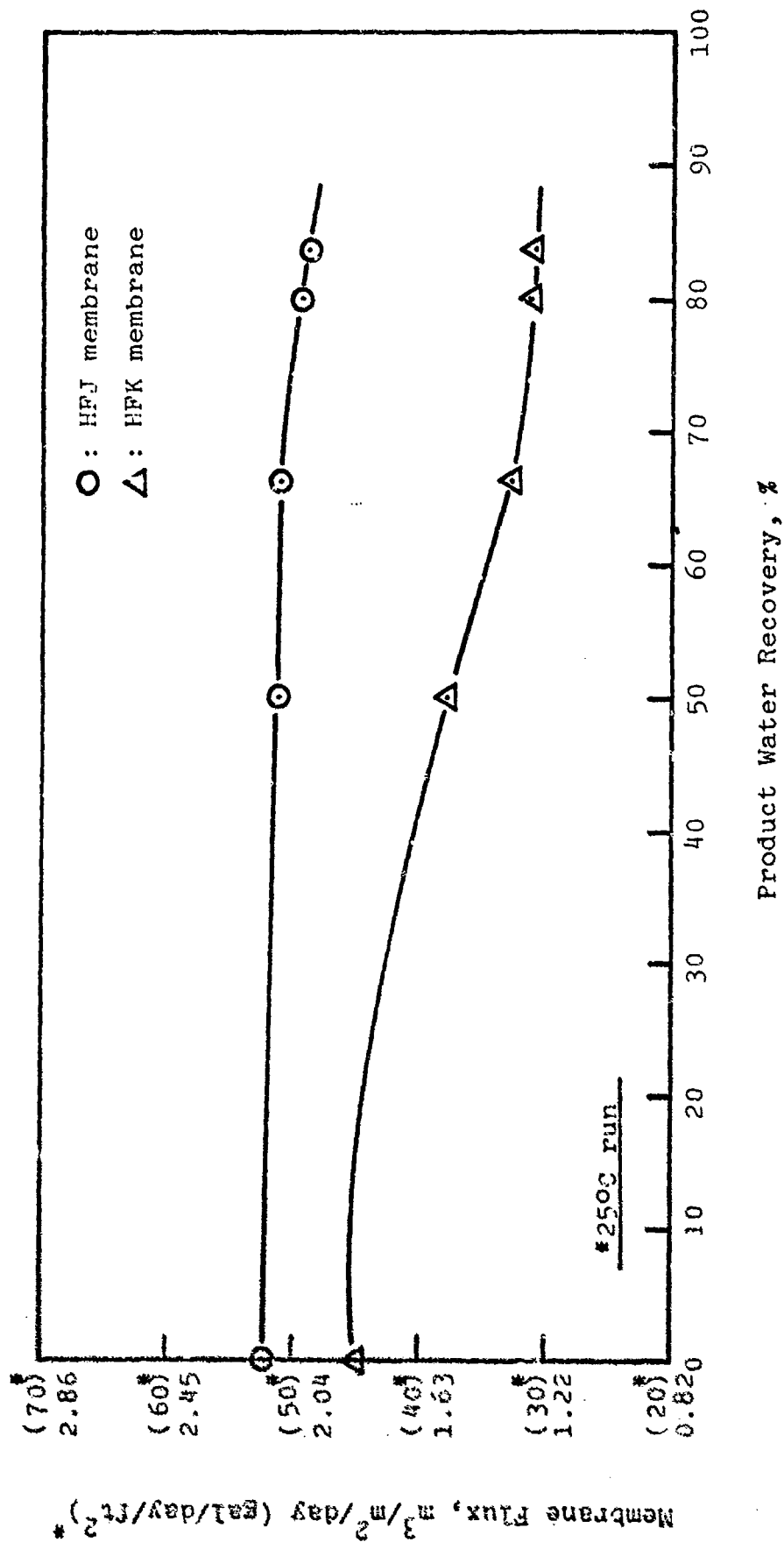


Figure 14. Ultrafiltration Membrane Performance (6% 3M FC-206 Solution with Tap-Water)

samples as well as membrane itself. The results of differential tests were summarized in Tables 16, 17 and 18. The dependence of membrane performance were evaluated in terms of both membrane flux and permeate concentration under controlled temperature at a given feed concentration. By comparing Figures 15 and 16, an increase in surfactant transport and almost zero rejection of glycol were observed with the 6% Ansul tap-water feed operated at 50°C (Figure 16).

The differences in TOC values between 25°C and 50°C UF experiments as shown in Figures 15 and 16 are due to variations encountered during sample preparations. It is seen in Figures 15 and 17 that HFJ and HFK membranes appear to have similar performance on the transport of AFFF ingredients. Table 19 shows that the present treatment set up was slightly favorable to 3M FC-206 because of the comparatively low rejections. But, from the chemical composition standpoint, Ansul has a higher TOC value and surfactants present in the permeate than 3M FC-206.

Field tests at the Naval Research Laboratory (April 16, 1980) of the reconstituted AFFF using a 1:6 dilution of RO concentrate (6x) of Ansul showed that 45 seconds were required to extinguish 100% of the fire whereas the desirable time is 30 sec. In another test, the 1:6 diluted RO concentrate was spiked with 1.5% Ansul to account for the loss of surfactants during the recovery process, only 36 sec were required to put out the fire set by using 37.86 liters (10 gal) of aviation gasoline in a 2.6 square meter (28 square foot) fire fighting area. These experiments were performed using a 7.57 l/min (2 gal/min) nozzle

Table 16
Results of Membrane Study with 6% Ansul Solution
with HFJ and HPK Ultrafiltration Membranes (@ 25°C run)

<u>HFJ-Ultrafiltration Membranes</u>										
Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection		
	Glycol (%)	TOC (mg/l)	Surfactants* (foam, ml)	Flyx (m ³ /m ² /day)	Glycol (%)	TOC (mg/l)	Surfactants* (foam, ml)	Glycol (%)	TOC (%)	Surfactants* (%)
1. X	5.12	9,990	145	1.86	5.1	9,240	80	0.39	7.5	44.8
1.6X	5.2	9,590	170	1.87	4.9	10,240	95	5.77	--	44.1
2.6X	5.3	11,340	210	1.93	6.35	9,240	110	--	18.5	47.6
3.3X	6.	11,740	200	1.89	5.25	9,590	100	12.5	18.3	50.
4.6X	5.9	11,830	200	1.84	6.1	9,240	100	--	21.9	50.
<u>HPFK-Ultrafiltration Membranes</u>										
1. X	5.12	9,990	145	1.32	5.25	7,740	85	--	22.5	41.4
1.8X	5.2	9,590	170	1.09	5.	9,990	95	3.85	--	44.1
2.6X	5.3	11,340	210	1.14	5.75	9,590	100	--	15.4	52.4
3.3X	6.	11,740	200	1.13	5.55	8,740	85	7.5	25.6	57.5
4.6X	5.9	11,830	200	1.16	5.	9,240	90	15.25	21.9	55.

-- No Rejection

* Determined by Shake Test - 1:20 Dilution

Table 18

Results of Membrane Study with 6% 3M FC-206 Solution
with HFJ and HPK Ultrafiltration Membranes (@ 25°C run)

HFJ-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection		
	Glycol (%)	TOC (mg/l)	Surfactants (foam, ml)	Flux (m ³ /m ² /day)	Glycol (%)	TOC (mg/l)	Surfactants (foam, ml)	Glycol (%)	TOC (%)	Surfactants (%)
1.x	5.1	7,350	80	2.13	5.3	6,600	60	--	10.2	25.
2.x	5.48	6,600	100	2.09	6.4	6,000	65	--	9.1	35.
3.x	5.4	7,000	130	2.11	6.15	6,200	75	--	11.4	42.3
4.x	5.46	7,500	140	2.02	6.65	6,800	70	--	9.3	50.
5.x	5.37	8,500	145	1.99	6.63	7,000	75	--	17.6	48.3

HPK-Ultrafiltration Membranes

1.x	5.1	7,350	80	1.84	5.85	6,000	60	--	18.4	25.
2.x	5.48	6,600	100	1.54	N.D.	6,200	65	N.D.	6.1	35.
3.x	5.4	7,000	130	1.33	6.35	6,150	65	--	12.1	50.
4.x	5.46	7,500	140	1.28	5.78	6,350	70	--	15.3	50.
5.x	5.37	8,500	145	1.26	6.35	6,800	70	--	20.	51.7

* Determined by Shake Test - 1:50 Dilution

N.D. - Not Determined

-- No Rejection

Table 17

Results of Membrane Study with 6% Ansul Solution
with HFJ and HFK Ultrafiltration Membranes (@ 50°C run)

HFJ-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection		
	Glycol (%)	TOC (mg/l)	Surfactants (foam, ml)	* Flux (m ³ /m ² /day)	Glycol (%)	TOC (mg/l)	Surfactants (foam, ml)	Glycol (%)	TOC (%)	Surfactants (%)
1. x	5.36	7,490	150	4.03	5.45	7,090	115	--	5.3	23.3
1.8x	5.5	7,890	170	3.56	5.35	6,790	115	2.73	13.9	32.35
2.6x	5.64	8,090	195	3.44	5.3	7,190	95	3.64	11.1	51.28
3.3x	5.42	8,690	185	3.38	5.2	7,590	115	4.06	12.7	37.8
4.6x	5.4	9,190	180	3.32	5.3	7,490	115	1.85	18.5	36.1

HFK-Ultrafiltration Membranes

1. x	5.36	7,490	150	2.73	5.25	6,990	110	2.05	6.7	26.67
1.8x	5.5	7,890	170	3.14	5.55	6,690	115	--	15.2	32.35
1.6x	5.64	8,090	195	2.97	5.7	6,790	110	--	16.1	43.59
3.3x	5.42	8,690	185	2.90	5.48	6,590	110	--	24.2	40.54
4.6x	5.4	9,190	180	2.84	5.4	6,890	95	--	25.	47.2

-- No Rejection

* Determined by Shake Test - 1:20 Dilution

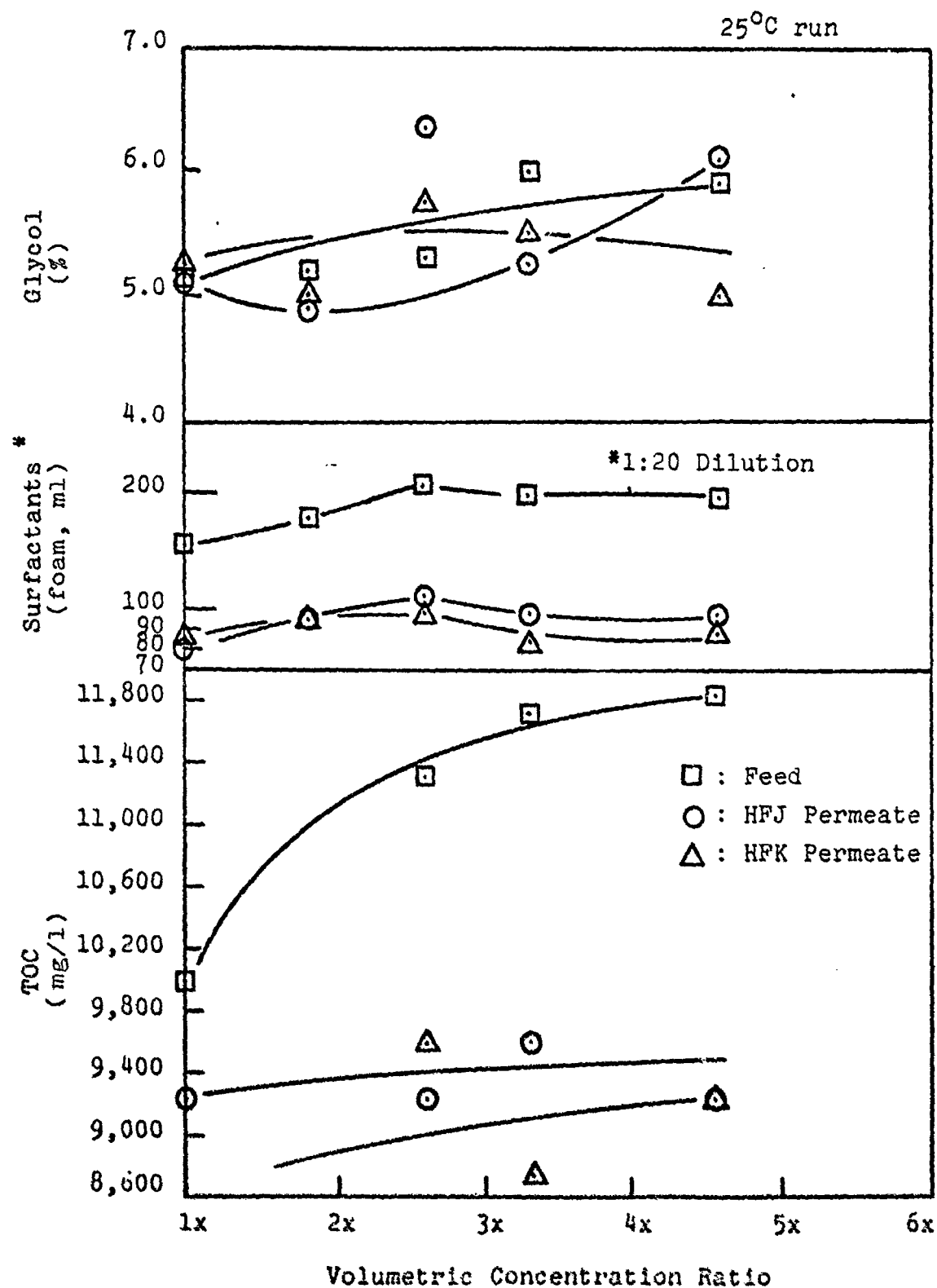


Figure 15. Ultrafiltration Membrane Performance of Ansol Constituents Transport at 25°C Run (6% Ansol Solution with Tap-water)

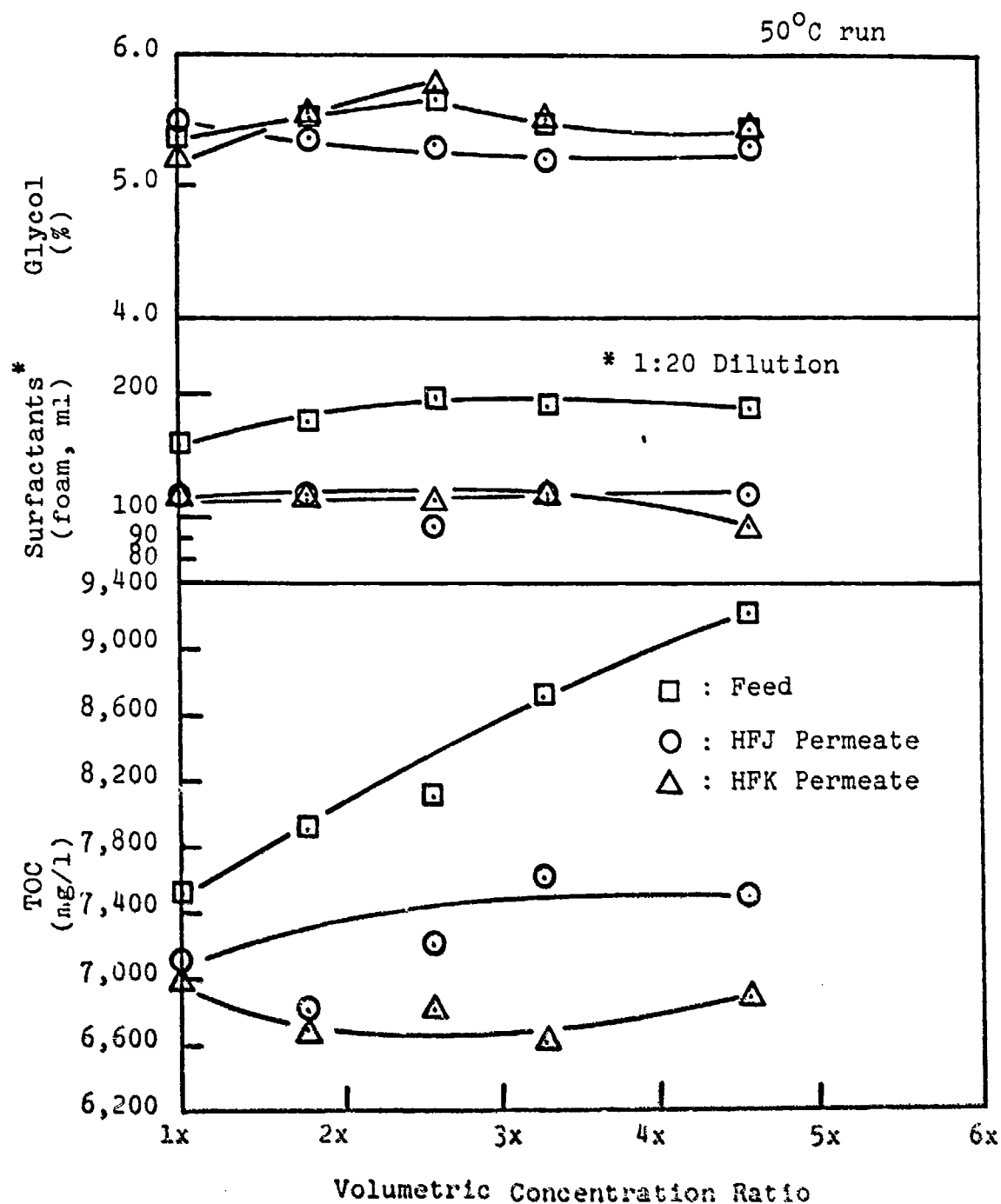


Figure 16. Ultrafiltration Membrane Performance of Ansol Constituents Transport at 50°C Run (6% Ansol Solution with Tap-Water)

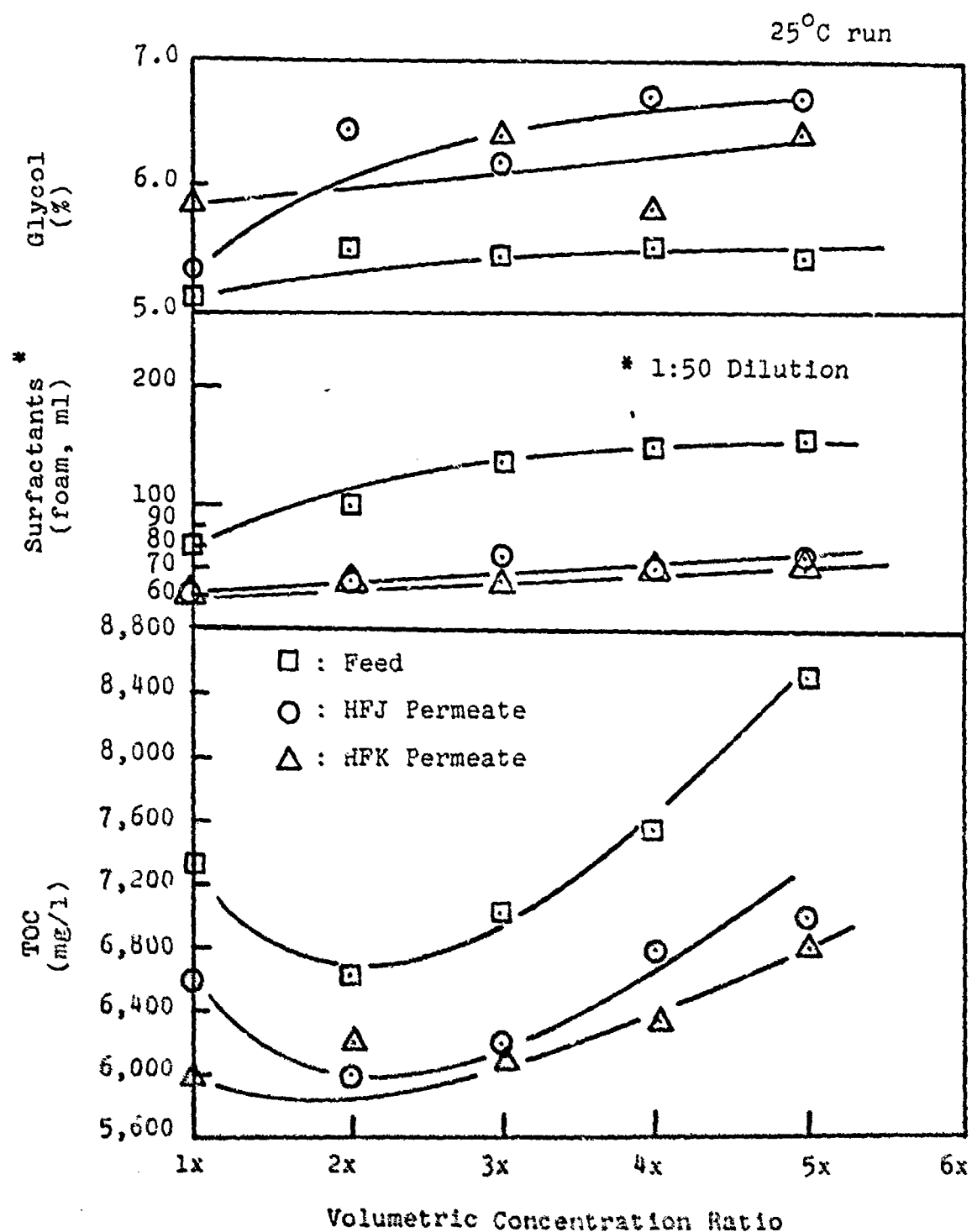


Figure 17. Ultrafiltration Membrane Performance of 3M FC-206 Constituents Transport at 25°C Run (6% 3M FC-206 Solution with Tap-Water)

Table 19

Overall Rejections of HFJ & HFK
Ultrafiltration Membranes Study with
.6% AFFF Tap-Water Solution

AFFF Sample	Overall Rejections, (%)			PWR, % *
	Glycol	TOC	Surfactants	
Ansul	0	15.6	26.67	78.33
3M-FC 206	0	12.8	12.95	80.00

* PWR - Product Water Recovery

flow rate at a nozzle pressure of 6.8 atm (100 psig). The burnback time at 25% burnback was 3 min with the 1:6 dilution of RO concentrate whereas the desired time is 5 min. The prevailing high wind (15 miles per hour) on the day of the testing was believed to impede the satisfactory performance of the reconstituted AFFF. However, the film and seal tests conducted indoors showd no ignition. In general, the initial results of field tests using the reconstituted AFFF were encouraging. Further tests with the RO concentrates obtained from spiked AFFF wastewater are therefore warranted.

The permeates from the UF experiments were processed as described previously. Tables 20 and 21 summarize the results in the differential tests, and Table 22 gives the overall performance of the reverse osmosis process. Over 99% rejection of TOC and surfactants was obtained with Ansul, and 97% and 98.7% rejection of TOC and surfactants, respectively, were observed with 3M FC-206. As can be seen from Figure 18, Ansul gives a higher membrane flux than 3M FC-206 with respect to product water recovery.

Both Ansul and 3M FC-206 RO concentrates give a linear increase in TOC, % of glycol and surfactant with respect to volumetric concentration ratio (Figure 19). In view of its good retention of the AFFF active ingredients, RO appears to have merit in concentrating the UF permeate for reuse of the AFFF solution. The RO permeate (Figures 20 and 21) contains a relatively low level of AFFF constituents. However, prior to discharging into the receiving stream, it may require additional

Table 20

Results of Membrane Study with 6% Ansul
Solution from UF Permeate

Dupont B-10 R.O. Module

Approx. Conc. Ratio	Feed Samples			Permeate Samples			Local Rejection			
	Glycol (%)	TOC (mg/l)	Surfactants (foam,ml)	Flux (m ³ /day)	Glycol (%)	TOC (mg/l)	Surfactants (foam,ml)	Glycol (%)	TOC (%)	Surfactants (%)
1. X	5.4	5,984	60 (1:50)*	6.45	0.11	27.8	20	98	99.54	99.3
1.8X	9.57	11,715	60 (1:90)	5.99	0.09	41.8	20	99.1	99.64	99.6
2.5X	11.42	16,665	65 (1:125)	5.36	0.12	71.3	20	98.9	99.57	99.8
3.2X	15.7	20,360	50 (1:160)	5.07	0.22	82.8	20	98.6	99.59	99.8
3.8X	N.D.	29,150	60 (1:190)	4.61	N.D.	90.	20	N.D.	99.69	99.8
6.3X	27.5	32,945	60 (1:315)	4.44	0.28	112.5	20	99.	99.66	99.9

N.D. - Not Determined

* Dilution Ratio

Table 22

Results of Reverse Osmosis Study with
6% AFFF Solution from Ultrafiltration
Permeate

AFFF Sample	<u>Overall Rejections, (%)</u>			PWR, % *
	Glycol	TOC	Surfactants	
Ansul	98.9	99.0	99.7	84.1
3M FC-206	98.3	98.	99.5	83.3

*PWR - Product Water Recovery

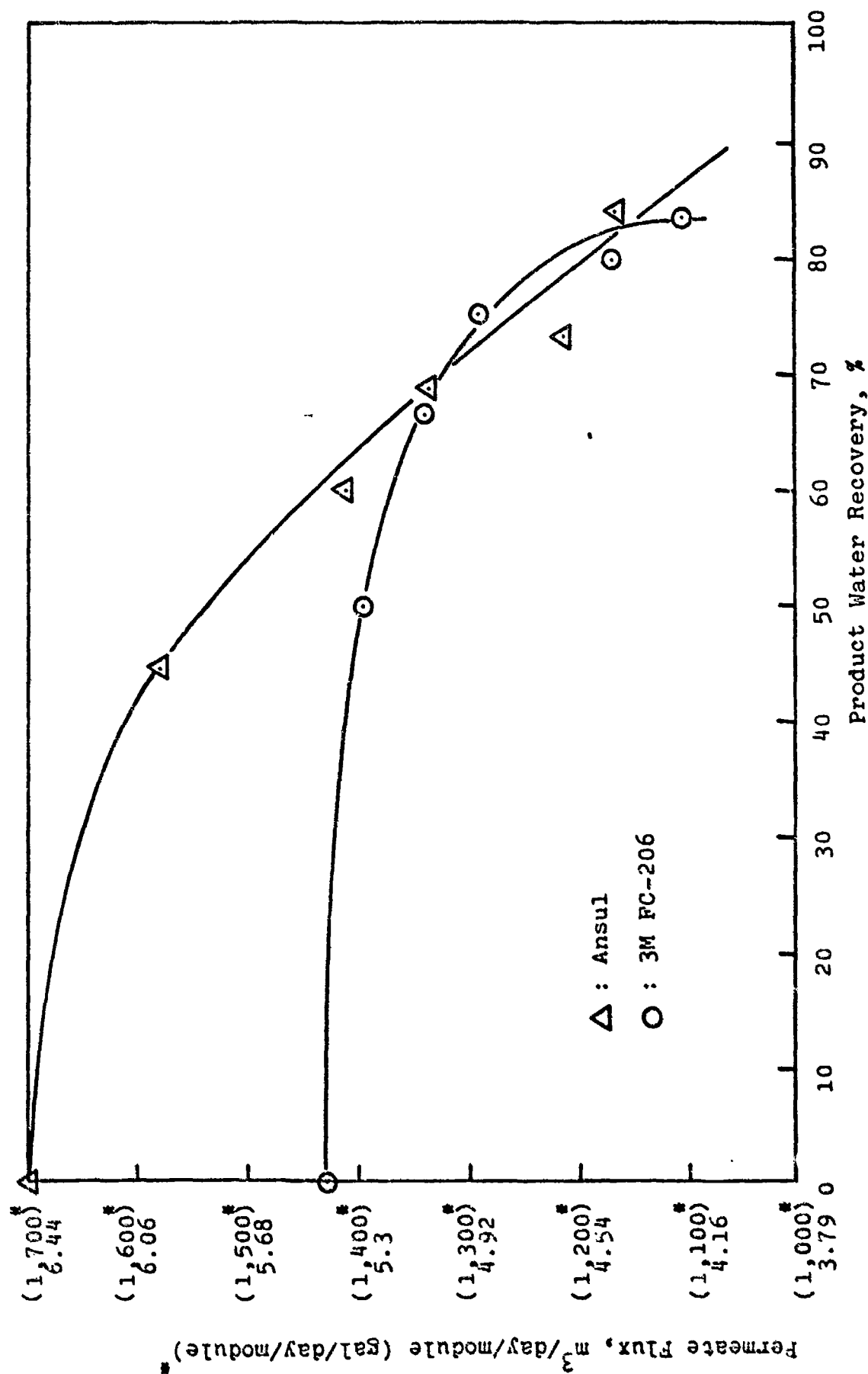


Figure 18. Reverse Osmosis Membrane Performance as a Function of Product Water Recovery (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study)

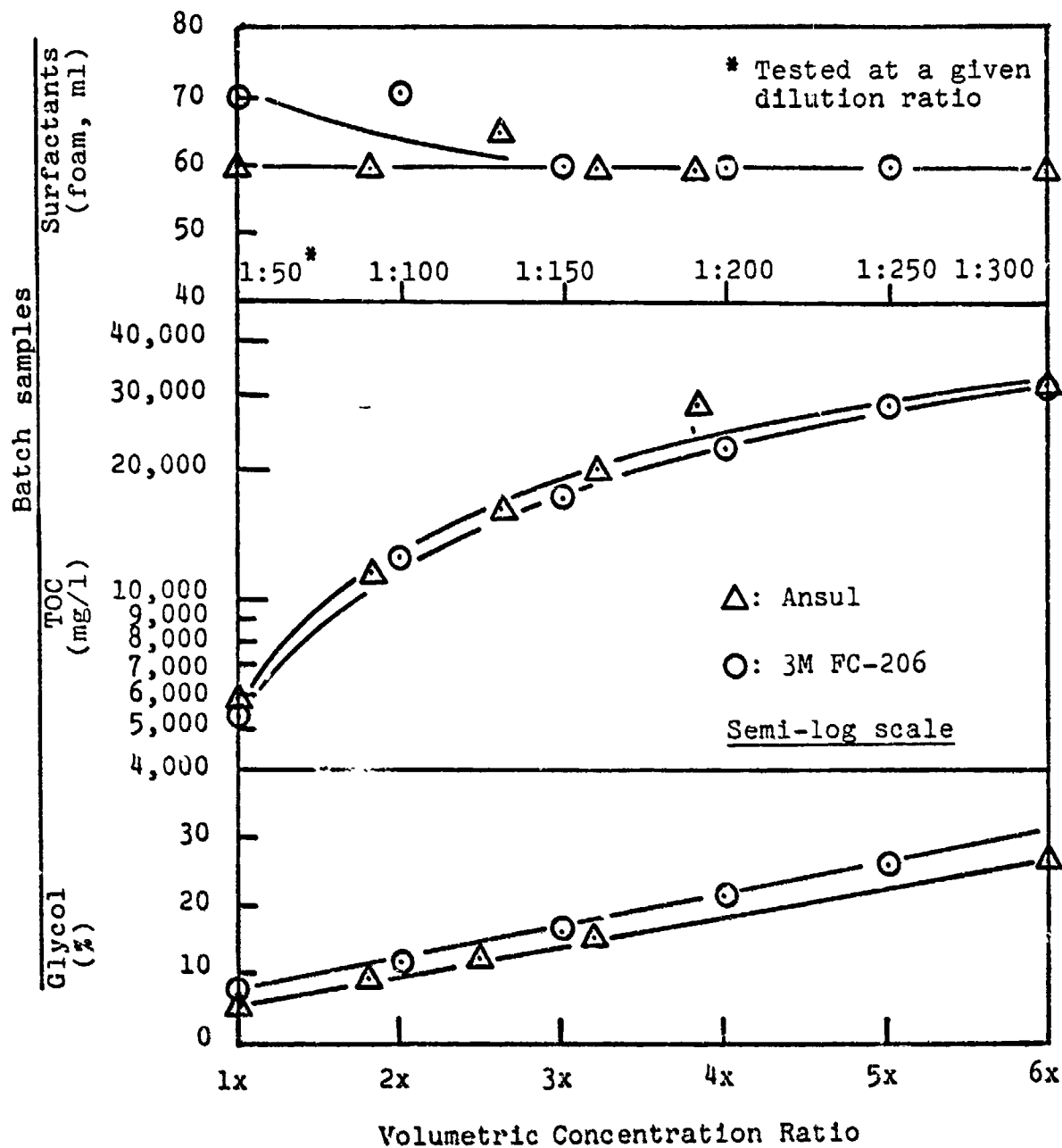


Figure 19. Relationships between Reverse Osmosis Concentrate and Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study)

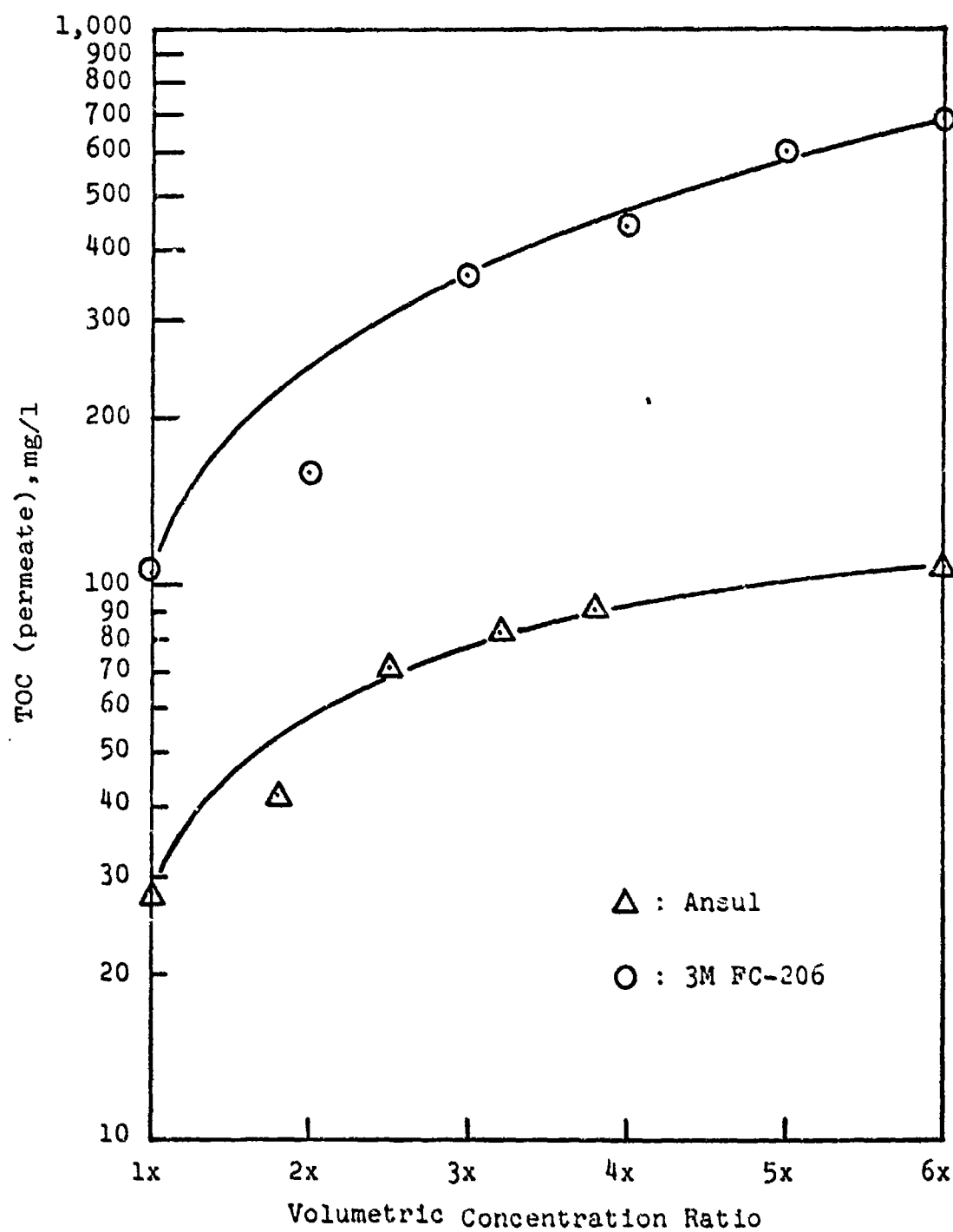


Figure 20. Reverse Osmosis Membrane Performance of AFFF Constituents Present in the Permeate as a Function of Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study)

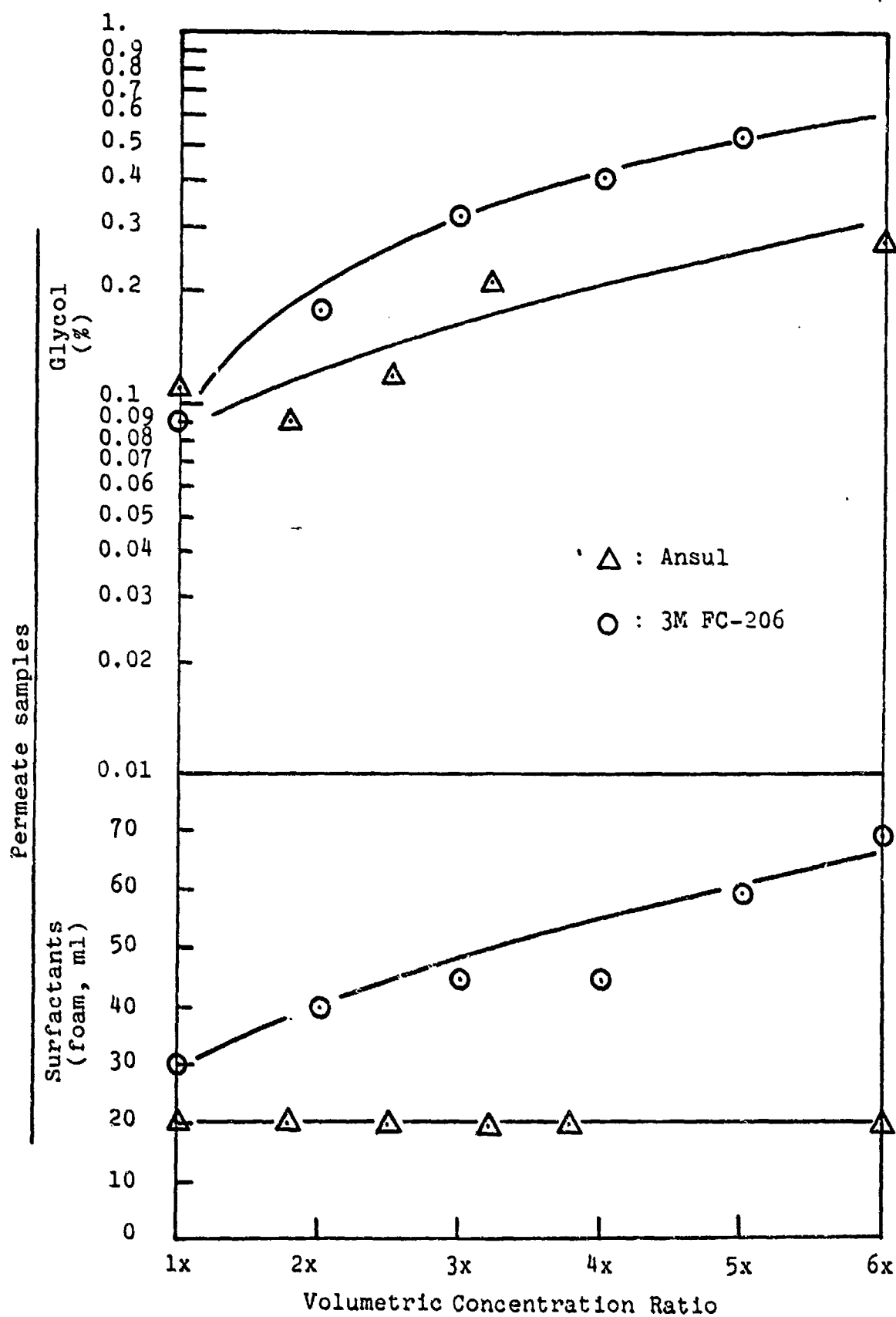


Figure 21. Reverse Osmosis Membrane Performance of AFFF Constituents Present in the Permeate as a Function of Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate AFFF Tap-Water Study)

treatment and its level of AFFF should be low enough for conventional biological treatment processes.

Although the RO process (DuPont B-10 permeator) is technically feasible for the recovery and reuse of both Ansul and 3M FC-206 AFFF, however, the presence of a higher concentration of 3M FC-206 constituents in the RO permeate (Figures 20 and 21), renders Ansul to be more environmentally acceptable in terms of disposals of the RO permeate.

Final (Fourth) Phase Experiment with 6% Spiked Wastewater Study

Two 55-gallon samples from the direct discharge of an actual fire fighting exercise were obtained from Warner-Robbins Air Force Base. This phase of study was carried out similar to the second phase experiment, with the exception that the wastewater was spiked with a 6% AFFF instead of a 3% AFFF concentrate. The purpose of this study was to make a comparison with the third phase experiment using a 6% AFFF tap-water study. The treatment of the direct discharge wastewater with the ultra-filtration process showed a consistent rejection of TOC and glycols as observed with the 6% AFFF solution (Table 23). The differential tests are summarized in Tables 24 and 25 and graphically illustrated in Figure 22. Again, they showed that HFJ and HFK UF membranes had similar performance. A comparison with feed samples and permeate samples showed that majority of the AFFF active ingredients were passed through the UF membrane (Tables 19 and 23). Higher rejection of surfactants may be due to the presence of wastewater containing other foreign constituents such as fuel, etc. which might tie up the foaming agent in the feed stream. From

Table 23

Performance of Ultrafiltration and Reverse
Osmosis Processed in Treating 6% AFFF Spiked
Fire Fighting Exercise Wastewater from
Warner-Robbins Air Force Base

1st Drum 6% 3M-FC 206 Spiked Wastewater

Parameter	Overall Rejection, %	
	Ultrafiltration*	Reverse Osmosis*
Glycol	3.39	96.75
TOC	9.32	96.14
DS	18.18	98.22
Surfactants	25.00	99.00

2nd Drum 6% Ansul Spiked Wastewater

Glycol	0	98.86
TOC	17.30	99.30
DS	7.79	97.93
Surfactants	33.33	99.33

* 83.3% Product Water Recovery

Table 25

Results of HFJ and HFK Ultrafiltration Membranes Study
with 6% 3M FC-206 Spiked Fire Fighting Training Exercises
Wastewater from Warner-Robbins Air Force Base (@ 50°C run)

HFJ-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples				* Flux (m ³ /m ² /day)	Permeate Samples				* TDS Surfactants (foam, ml)	Local Rejection			
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (foam, ml)		Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (foam, ml)		Glycol (%)	TOC (%)	TDS (%)	Surfactants (%)
1.x	5.9	8,580	550	80	2.02	5.9	8,480	465	55	--	1.17	15.5	31.25	
2.x	6.	8,980	550	95	2.61	5.7	8,985	480	60	5.	5.57	12.7	36.84	
3.x	5.9	9,980	575	100	2.37	5.5	8,485	485	60	6.78	10.98	15.7	40.	
4.x	6	10,780	600	105	2.35	6.1	8,785	510	60	--	18.51	15.	42.88	
6.x	6.4	12,480	650	130	2.25	6.	8,785	550	60	6.67	29.61	15.4	53.85	

HFK-Ultrafiltration Membranes

1.x	5.9	8,580	550	80	2.19	5.6	8,185	465	55	5.08	4.6	15.5	31.25
2.x	6.	8,980	550	95	2.02	5.6	8,785	450	55	7.33	8.85	18.2	42.11
3.x	5.9	9,980	575	100	1.89	5.7	8,685	455	60	3.38	12.98	20.9	40.
4.x	6.	10,780	600	105	1.95	5.7	8,885	465	60	5.	17.58	22.5	42.84
6.x	6.4	12,480	650	130	2.02	5.7	8,785	490	60	10.94	29.61	24.6	53.85

-- No Rejection

* Determined by Shake Test - 1:50 Dilution

Table 24

Results of HPJ and HPK Ultrafiltration Membranes Study
 with 6% Ansol Spiked Fire Fighting Training Exercises
 Wastewater from Warner-Robbins Air Force Base (@ 500C run)

HPJ-Ultrafiltration Membranes

Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection		
	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l)	Flux (m ³ /m ² /day)	Glycol (%)	TOC (mg/l)	TDS Surfactants* (mg/l)	Glycol (%)	TOC (%)	TDS Surfactants* (%)
1.x	5.76	7,420	488	90	3.14	6.6	6,860	425	65	8.29 12.9 27.78
2.x	5.76	8,100	480	85	3.20	6.6	6,230	430	65	23.09 10.4 23.53
3.x	5.9	8,480	490	110	3.02	6.1	6,000	450	65	29.25 8.2 40.91
4.x	6.	9,480	550	115	2.90	6.4	6,600	460	65	30.38 16.4 43.48
6.x	6.1	9,980	580	120	2.73	6.4	6,980	475	65	30.06 18.1 45.83

HPK-Ultrafiltration Membranes

1.x	5.76	7,480	488	90	2.37	6.5	6,580	385	65	12.03 21.1 27.78
2.x	5.76	8,100	480	85	2.37	6.4	6,380	400	65	21.23 16.7 23.53
3.x	5.9	8,480	490	110	2.31	6.4	6,380	410	65	24.76 16.3 40.91
4.x	6.	9,480	550	115	2.18	6.	6,380	425	65	32.7 22.7 43.48
6.x	6.1	9,980	580	120	2.13	6.4	6,580	435	65	34.07 25. 45.83

-- No Rejection

* Determined by Shake Test - 1:50 Dilution

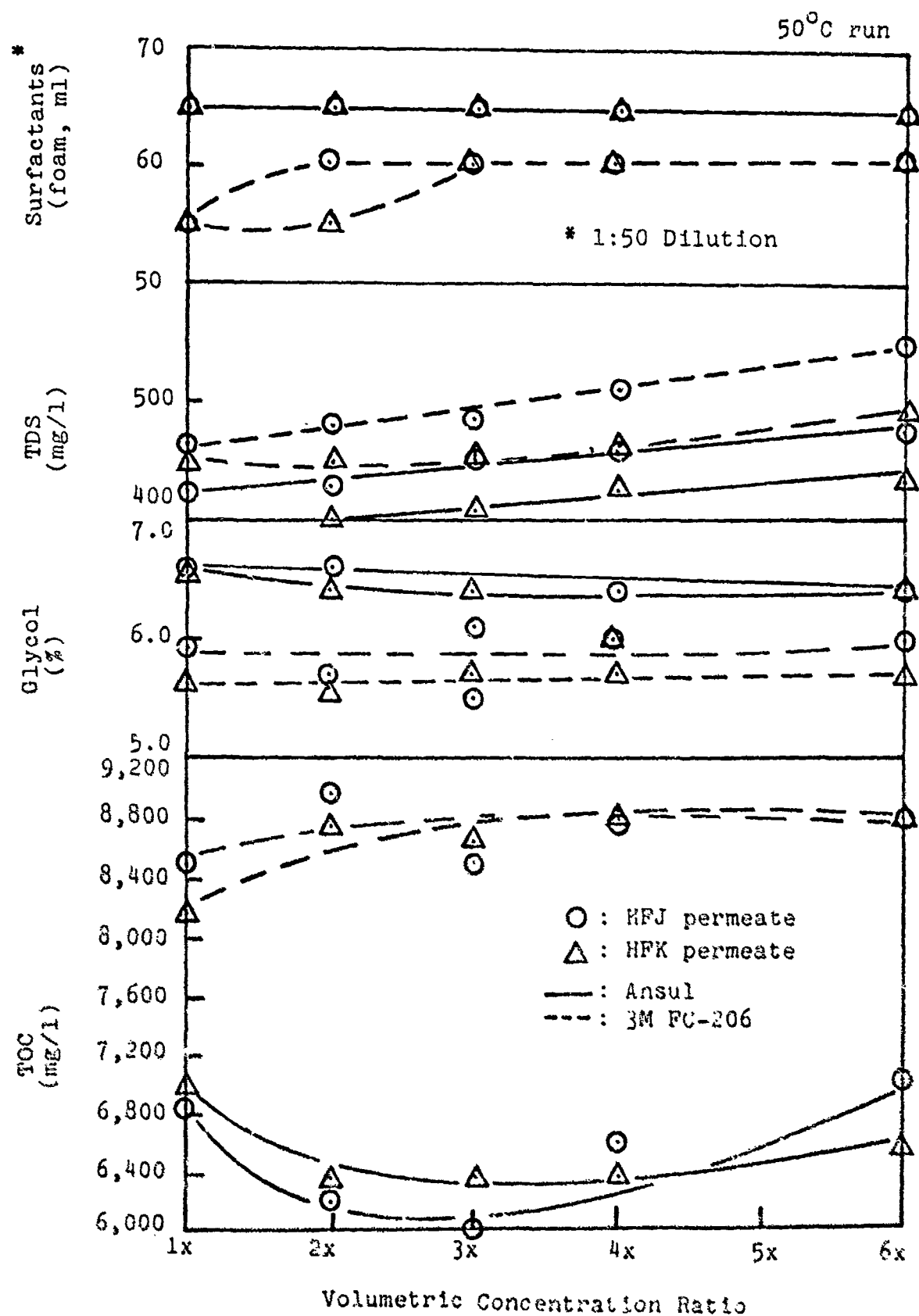


Figure 22. Ultrafiltration Membrane Performance of AFFF Constituents Transport (6% AFFF Spiked Wastewater)

physical observations of the ultrafiltrate it was apparent that the majority of the wastewater impurities, such as oil emulsions and suspended solids, were rejected by the UF membrane. The greatest difference was a decrease in the membrane flux with the wastewater samples (see Figures 13 and 23).

The permeate from the UF experiment run at 50°C was saved and used as the feed solution for the RO process as described previously. The results of the RO treatment of UF permeate were comparable to that obtained with the 6% AFFF solution (compare Figures 19, 20 and 21 with Figures 24, 25 and 26, see Tables 26 and 27).

One of the objectives of evaluating the RO process is to achieve a 10-fold volume reduction in the holding tank. Since there are limitations in the system employed in this study, the desired volume reduction could not be achieved. Membrane fluxes obtained with wastewater experiment (Fig. 27) were somewhat lower than that obtained with the 6% AFFF tap-water study (Figure 18). However, the major concern with the use of the membrane processes is the rejection of the AFFF active ingredients, especially, the surfactants, by the ultrafiltration process. Therefore, a minimum of 25% of the fresh AFFF, or preferable 1/3 of it, should be supplemented while considering reuse of the RO concentrates. Finally field test of the RO concentrate recovered from this phase of the study should be completed by the Naval Research Laboratory sometime in September 1980.

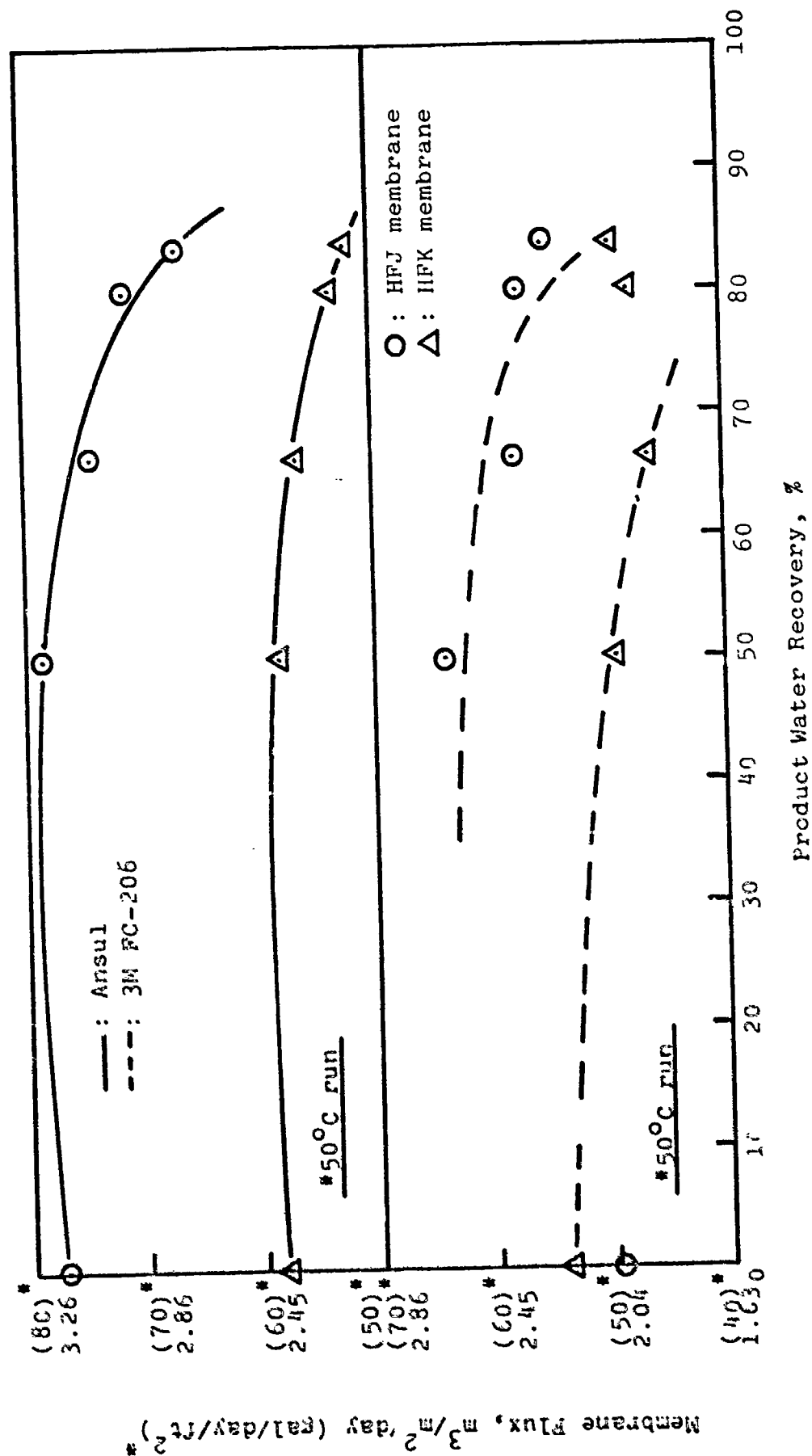


Figure 23. Ultrafiltration Membrane Flux as a Function of Product Water Recovery (6% APFF Spiked Wastewater)

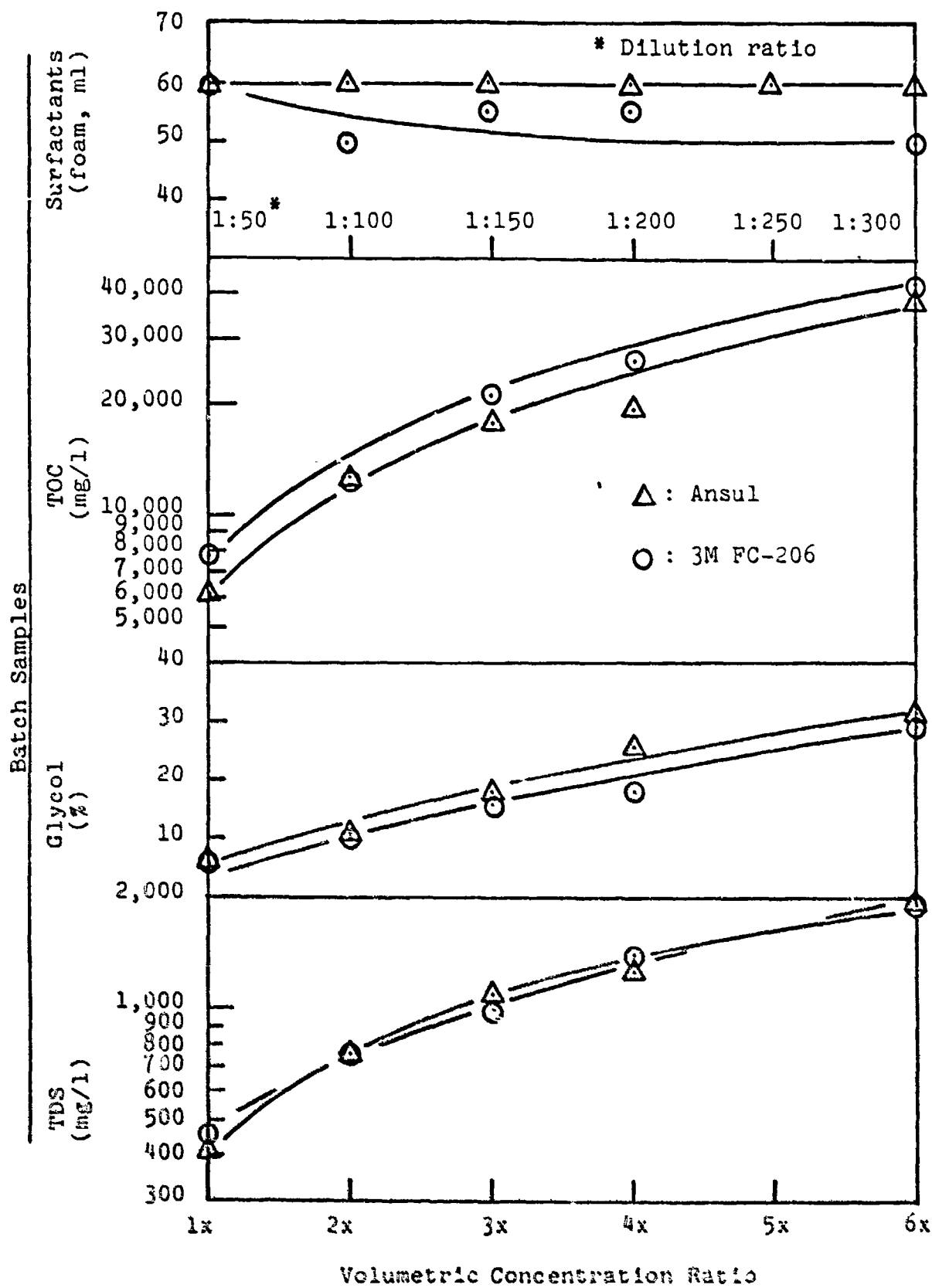


Figure 24. Relationships between Reverse Osmosis Concentrate and Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% AFPF Spiked Wastewater)

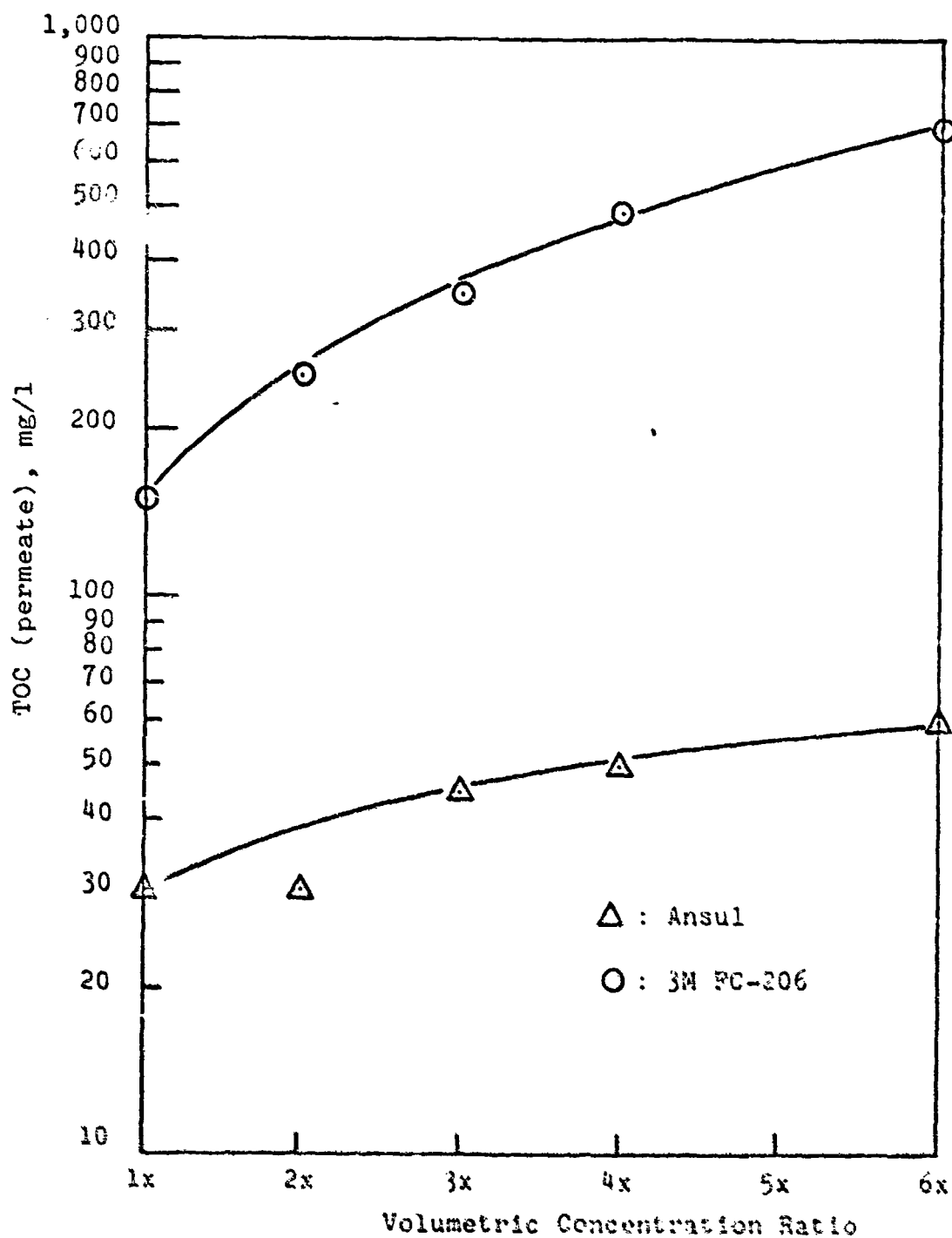


Figure 25. Reverse Osmosis Membrane Performance of APFP Constituents Present in the Permeate as a Function of Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% APFP Spiked Wastewater)

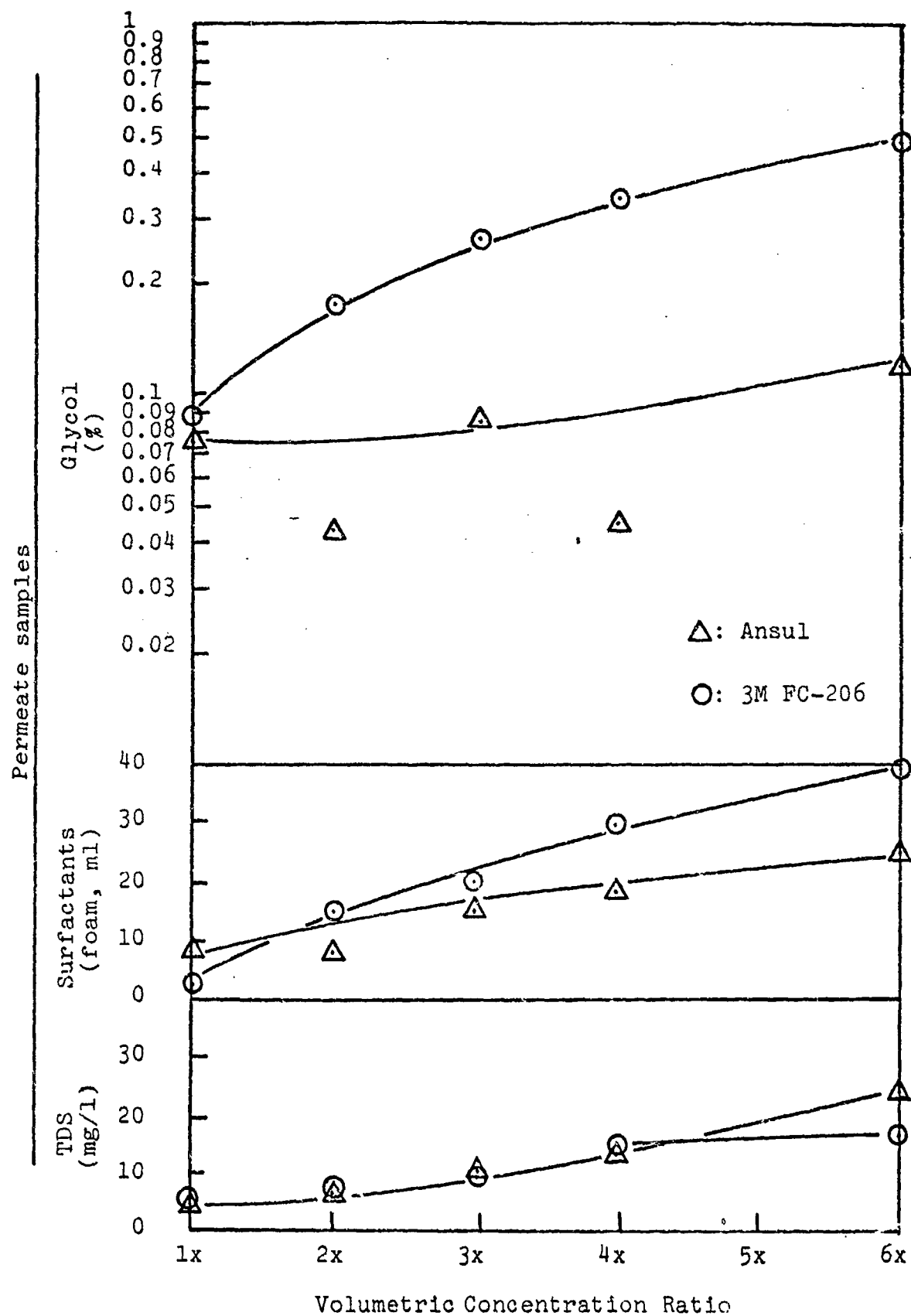


Figure 26. Reverse Osmosis Performance of AFFF Constituents Present in the Permeate as a Function of Volumetric Concentration Ratio (Feed Solution from Ultrafiltration Permeate 6% AFFF Spiked Wastewater)

Table 26
Results of Du Pont Reverse Osmosis B-10 Module Study
with 6% Ansol Spiked Fire Fighting Training Exercises
Wastewater Solution from Ultrafiltration Permeate

Approx. Conc. Ratio	Feed Samples				Permeate Samples					Local Rejection			
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (foam, ml)	Flux (m ³ /day)	Glycol (%)	TOC (mg/l)	TD ₃ (mg/l)	Surfactants (foam, ml)	Glycol (%)	TOC (%)	TDS (%)	Surfactants (%)
1.x	6.5	6,185	410	60 (1: 50)*	5.55	0.075	30	5.0	8	98.85	99.51	98.8	99.73
2.x	10.5	12,725	750	60 (1:100)	5.12	0.043	30	7.0	8	99.59	99.76	99.1	99.87
3.x	17.5	17,645	1,080	60 (1:150)	4.72	0.085	45	10.5	15	99.51	99.74	99.0	99.83
4.x	25.0	18,960	1,230	60 (1:200)	4.37	0.045	50	13.5	18	99.82	99.74	98.9	99.85
6.x	31.0	36,950	1,950	60 (1:300)	3.54	0.12	60	24.0	25	99.61	99.84	98.8	99.86

* Dilution Ratio

Table 27
Results of Du Pont Reverse Osmosis B-10 Module Study
with 6% 3M FC 206 Spiked Fire Fighting Training Exercises
Wastewater Solution from Ultrafiltration Permeate

Approx. Conc. Ratio	Feed Samples			Permeate Samples				Local Rejection		
	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (foam, ml)	Flux (m ³ /day)	Glycol (%)	TOC (mg/l)	TDS (mg/l)	Surfactants (foam, ml)	Surfactants (%)
1.x	5.7	7,780	450	60 (1:50)	5.32*	0.088	150	4.8	2.0	98.46 98.07 98.93-99.93
2.x	9.84	11,980	750	50 (1:100)	5.27	0.175	250	7.8	15.0	98.22 97.91 98.96 99.7
3.x	15.25	20,970	975	55 (1:150)	5.14	0.265	350	9.8	20.0	98.26 98.33 98.99 99.27
4.x	17.5	25,970	1,400	55 (1:200)	4.63	0.337	490	12.8	35.0	98.07 98.11 99.09 99.68
6.x	28.5	41,960	1,980	50 (1:300)	4.54	0.485	690	17.0	40.0	98.26 98.36 99.14 99.73

* Dilution Ratio

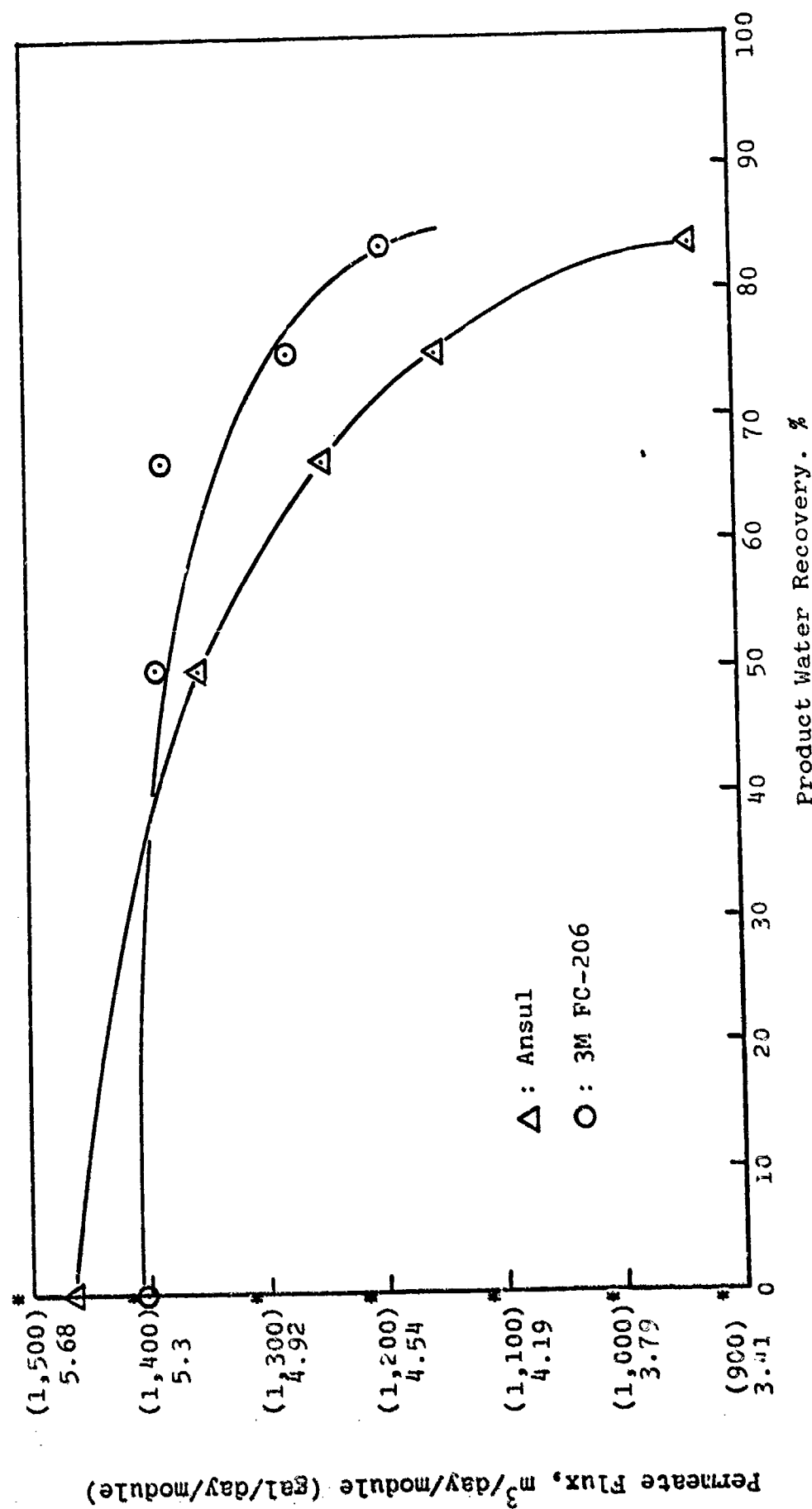


Figure 27. Reverse Osmosis Membrane Performance as a Function of Product Water Recovery (Feed Solution from 6% AFFF Spiked Wastewater)

V. PROCESS ECONOMICS

Based on the results of a study on the 6% spiked wastewaters generated from the fire fighting facility at Warner-Robbins AFB, an attempt has been made to estimate the treatment costs for a 189.3 cu meter per day (50,000 gpd) plant. Figure 28 depicts the proposed schematic flow diagram of the UF-RO treatment system receiving wastewater from the direct discharge of a fire fighting facility. The ozonation serves the purposes of both disinfection and final polishing of the treated effluents. Because of the high costs normally associated with the use of ozone for final polishing of TOC (approximately 25 mg O_3 /mg TOC removed), the ozonation step, as shown by the dotted lines in Figure 28, is incorporated only as an option.

The cost estimate for the membrane processes is based on the treatment of the fire fighting wastes with a minimum provision given to the ultimate disposal of the ultrafiltration retentate using drying lagoons. The flux data used in the design were $1.632 \text{ m}^3/\text{m}^2/\text{day}$ (40 gal/ft²/day) for the UF module lined with HFJ membrane and 11.358 cu meter per day (3000 gal/day) for the DuPont B-10 permeator (5' x 5" dia.).

A more conservative approach has been taken in estimating the costs of the membrane treatment process. This is reflected by the use of a contingency factor of 30% and the use of 8% straight-line on capital costs (Table 28). It is seen from Table 28 that treatment costs are approximately \$1.85/cu meter (\$7/1000 gal).

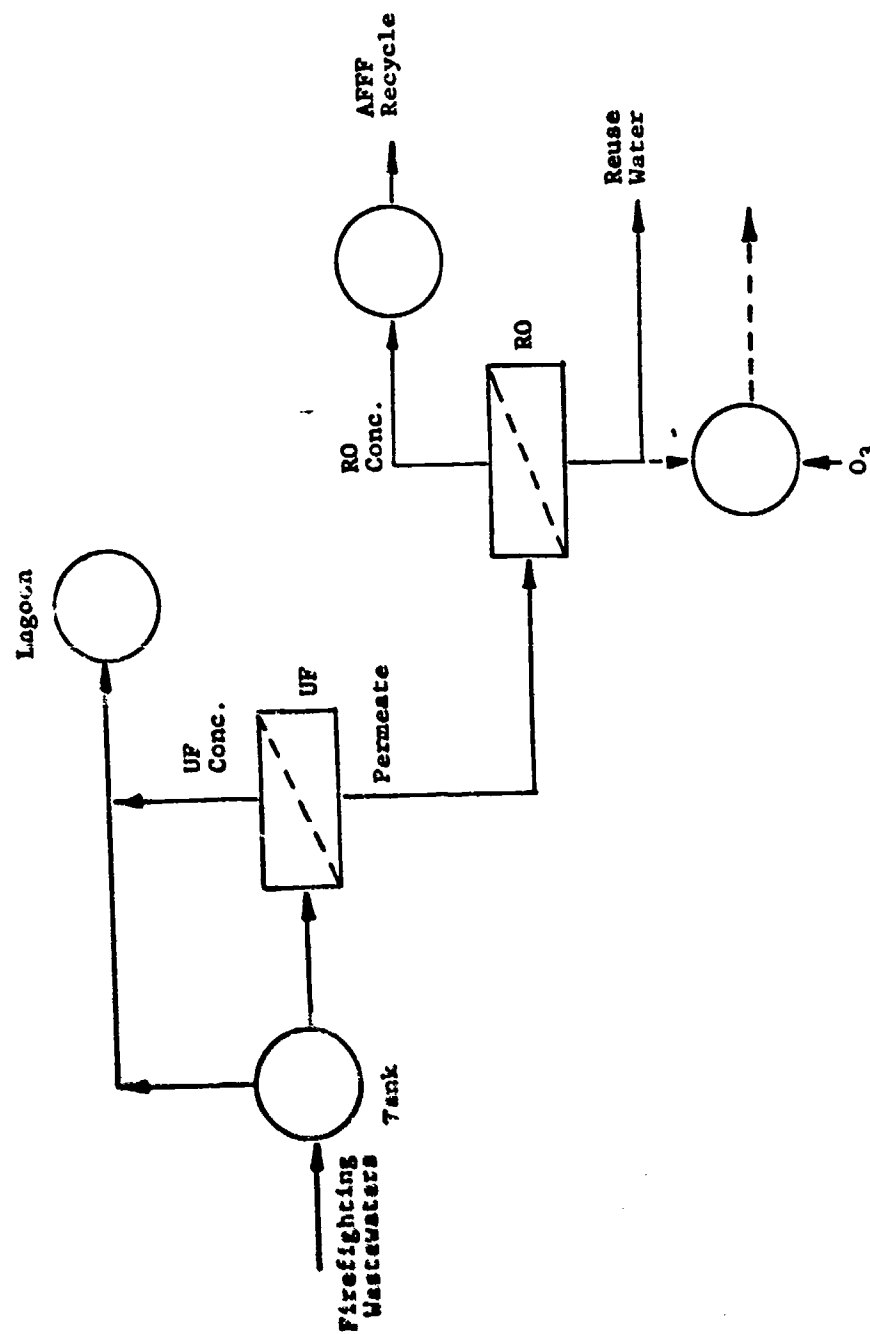


Figure 28. Proposed Membrane Treatment System for AFFF Wastewater

Table 28
Estimated Capital and Operating Cost of the
Proposed Membrane Treatment System (Figure 28)
Basis: 189.3 m³/day (50,000 gpd) 300 days/yr, 22 hrs/day

Capital Costs	
Storage Tank, 18.93 m ³ (5000 gal)	\$ 4,000
Ultrafiltration, 116.13 m ³ (1250 ft ²) @ \$753.47/m ²	169,000 ⁺
Reverse Osmosis @ \$396.2/m ³ /day (\$1.5/gal/day)	82,000
Drying Lagoon	7,000
Pipings	8,000
Engineering Fee	20,000
Subtotal A	<u>\$290,000</u>
Contingencies, 15% of Subtotal A	43,500
	<u>\$333,500</u>

Operating Costs	
Electricity (50 H.P.) @ 4¢/KWH	\$ 10,800
Chemicals	
Cleaning compounds	500
Labor (Avg 4 hr/day) @ \$8/hr + 40% OH	13,500
Maintenance, 3% of Capital Costs	10,000
Interest, 8% of Capital Costs	26,680
Taxes and Insurances, 3% of Capital Costs	10,000
Membrane Replacement (20% of Module Costs)*	18,340
Depreciation (10-yr Straight Line on Capital Costs Less Modules)	19,800
	<u>\$109,620</u>

Treatment Costs

$$\begin{aligned}
 \frac{109,620}{50,000 \times 300} &= \$0.00731/\text{gal} \\
 &= \$7.31/1000 \text{ gal} \\
 &= \$5.60/100 \text{ ft}^3 \\
 &= \$1.93/\text{m}^3
 \end{aligned}$$

Make-up water charge varies from \$0.07-0.78/m³ (\$0.2-2.2/100 ft³)
depending upon locations and accompanying sewer charges

*UF modules costs are approximately 30% of the capital costs for the membrane equipment and 50% for the RO equipment.

⁺See the manufacturer's quotation in Appendix II.

The credit that can be realized by recovering the RO retentate to supplement the AFFF concentrate is estimated based on a 90% recovery for both UF and RO processes and 80% for the AFFF active constituents. This results in approximately 72% recovery of the AFFF constituents at a final concentration of approximately a half of the original 6% AFFF concentrate. Assuming that a half of the RO retentate that will be used to supplement the AFFF concentrate, this amounts to an annual saving of 1249.38 cu meter (330,000 gallons) of AFFF concentrate. Depending upon the price of the AFFF concentrate, the capital costs of the treatment process can be returned in a relatively short period of time. For example, a return on investment in two month can be realized if the AFFF costs \$1.32/l (\$5 per gallon). In addition, the RO permeate is of a high quality water containing extremely low levels of total dissolved solids (TDS) which can be used as the makeup water for the fire fighting exercises in order to reduce the build-up of TDS in the recovery system.

Comparable process economics have been realized with other membranes processes as given in Appendix I. These are obtained based on more than 150 plants' operation using the membrane processes in recovery by products of value from their product or waste streams.

XI. CONCLUSIONS

The primary goal of this research was to demonstrate the feasibility of recovery of AFFF active ingredients with ultrafiltration and reverse osmosis membrane processes. Based on the results of this research study, it is obvious that membrane treatment is technically feasible for recovery and reuse of AFFF ingredients from fire fighting wastewaters. The following conclusions can be made from this research:

1. Membrane treatment is applicable to all types of AFFF.
2. The type of AFFF and its chemical and physical properties influence membrane flux and rejection.
3. The type of UF membranes and its chemical and physical properties also influence treatment for various AFFF.
4. Abcor HFD, HFF, HFJ and HFK UF membranes have similar performance on 3M FC-206.
5. Abcor HFJ and HFK UF membranes gives better performance on Ansul than HFD and HFF UF membranes.
6. Membrane flux increases with increasing temperature and higher temperature also allows a better recovery of AFFF ingredients from the UF permeates.
7. The DuPont B-10 permeator gives an overall rejection of 97-99% AFFF active ingredients and appears to have merit in concentrating the UF permeate for reuse.

8. Results of this study indicate that, on an average, recovery of 75% of the key AFFF active ingredients as measured by the foam test was achieved.

XII. RECOMMENDATIONS

In view of the technical feasibility of the recovery and reuse of AFFF active ingredients with the UF/RO processes, and the favorable economics of the treatment process, it is recommended that a pilot-scale study be conducted. The specific tasks to be performed prior to and during the pilot-scale study are outlined in the following:

- A. The favorable results of Navy's tests on the AFFF materials recovered during the fourth phase of this study will be supportive.
- B. Upon favorable results obtained from such tests with the AFFF materials recovered from spiked wastewater, a 7.57 - to 18.9 cu meter (two- to five-thousand gallons per day) pilot-scale UF/RO system should be evaluated.
- C. Optimum recovery of AFFF active ingredients for both the UF and the RO treatment processes should be determined in order to establish means of reuse of the recovered AFFF materials.
- D. Consideration should be given to investigate concentration polarization effects and methods for reducing membrane fouling.
- E. A long-term continuous operation of the pilot-scale system for a period of at least six months should be carried out on-site using the actual fire fighting wastewaters.

- F. Quality control of the recovered AFFF materials should be established using either laboratory tests on AFFF active ingredients (e.g. foam test) or direct tests on its fire fighting efficiencies.
- G. A simple and reliable laboratory analytical instrument should be developed to monitor the quality of the recovered AFFF materials as compared with the AFFF concentrate received from the manufacturers.
- H. A refined economic analysis based on the information obtained from the pilot-scale investigation should be made.

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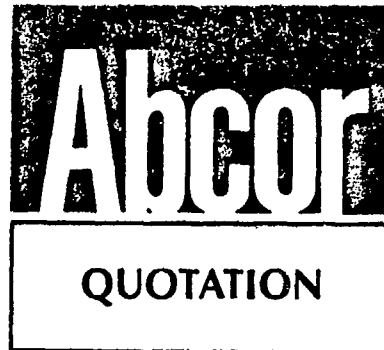
APPENDIX

- I. Payback periods for major applications of ultrafiltration
- II. Quotation on the 50,000 GPD ultrafiltration system

PAYBACK PERIODS FOR MAJOR APPLICATIONS OF ULTRAFILTRATION

<u>Industry</u>	<u>Application</u>	<u>Expected Payback Period</u>	<u>Reference</u>
Automotive	Recovery of Electrocoat Paint	1.24 Years	Abcor Brochure - AA/BR-79-5
Chemical	Concentration of Polymeric Lattices	0.47 Years	Abcor Bulletin - PIB 250
Textile	Size Recovery	1 to 2 Years	Hoffman, C. R., et al, "Application of Spiral-Wound Ultrafiltration for Recovery of Textile Desizing Effluent," March 21, 1979.
Food	Milk Concentration Prior to Cheese Making	0.69 Years	Abcor Brochure - FD/BR-78-10
Tannery	Recovery of Spent Unhairing Bath	2.93 Years	Kleper, M. H., "A New Approach for Treatment of Spent Tannery Liquors" June, 1979.
Tannery	Recovery of Vegetable Tannin	1.63 Years	Kleper, M. H., "A New Approach for Treatment of Spent Tannery Liquors," June, 1979.
Food	Soy Isolate Production	See Reference	Hensley, D. W., and Lawson, J. T., "Economic Evaluation of Soy Isolate Production by a Membrane Isolation Process," May, 1979.

Date: March 24, 1980
To: Georgia Institute of Technology



No. 80-3-058-A

Description:

Page 1

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM

SYSTEM DESCRIPTION

One Abcor UF-1000 FEM O/W Ultrafiltration System containing 456 Abcor 10-HFM-251 FNO tubular membranes, manifolded into 57 parallel passes of 8 tubes in series per pass. The total active membrane area is 1,000 sq. ft.

A. Abcor UF-1000 FEM O/W Ultrafiltration System includes:

- a. Two centrifigual pumps, (one cleaning pump and one circulation pump).
- b. Feed temperature gauge.
- c. Four pressure gauges.
- d. High temperature switch interl sked to circulation pump.
- e. Low pressure switch interlocked to circulation pump.
- f. High pressure switch interlocked to circulation pump.
- g. Permeate low flow switch interlocked to circulation pump.
- h. Cabinet pan high liquid level switch interlocked to circulation pump.
- i. Audio-visual alarms for Items d-h, above.
- j. Automatic purge sequence activated by circulation pump shutdown due to switches in Items d-h, above.
- k. Rotameter on permeate line.
- l. All valves, piping, and internal wiring for proper recommended operation.
- m. Cleaning tank and associated piping.
- n. Heat exchanger on feed line.
- o. One drum of Ultraclean detergent (250 lbs.).

Abcor**QUOTATION**

Date: March 24, 1980

To: Georgia Institute of Technology

No. 80-3-058-A

Description:

Page 2

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM

Overall dimensions of the proposed system are 32' long, 14' high, 10' wide. Ten feet of clearance must be allowed at one end of the unit. All components are skid-mounted.

The estimated weight of the entire system is 18,600 lbs. (operating) and 14,900 lbs. (shipping).

B. Additional Supply

In addition, Abcor will:

1. Provide three copies of a System Operating Manual with appropriate drawings.
2. Supply four working days of technical service for assistance during start-up of the equipment and operator training.
3. Supply six spare ultrafiltration membranes and parts kit.

C. Factory Testing

In order to minimize installation time, Abcor will preassemble and test the UF system in its own shop, then disassemble (as required), for easy shipment and installation at the plant site.

D. General Materials of Construction and System Components**1. Membrane Cabinet**

The membrane cabinet is constructed of carbon steel and finished inside and out with Sherwin Williams polyurethane paint.

2. Cleaning Tank

The cleaning tank is constructed of carbon steel. The interior will be sandblasted to white metal and finished with coal tar epoxy. The exterior will be chemically cleaned with Sherwin Williams surface prep and finished with Sherwin Williams polyurethane paint.

SPECIALISTS IN SEPARATION PROCESS TECHNOLOGY AND SYSTEMS
ABCOR INC., 850 MAIN STREET, WILMINGTON, MA 01887 (617) 657-4250

Abcor

Date: March 24, 1980

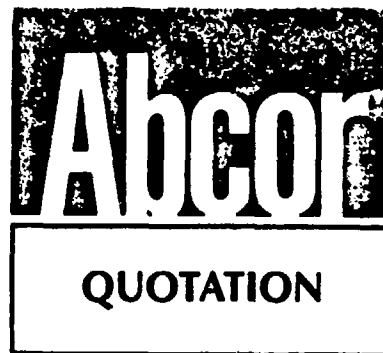
To: Georgia Institute of Technology

No 80-3-058-A

Description:

Page 3

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM



3. Pumps

The pumps are end-suction centrifugal type (all iron construction) with packing gland. Pumps are mounted on a baseplate and coupled to Standard NEMA frame TEFC motors. Replacement of either pump or motor is simple since a close-coupled pump is not used.

Pumps will be manufactured by either Carver, Worthington, Crane Deming, or equivalent.

4. Equipment Bedplate

The equipment bedplate is constructed of carbon steel and painted with Sherwin Williams polyurethane paint. Lifting pads and mounting holes are provided for ease of transportation and installation.

5. Piping

Feed, concentrate, circulation loop, and utility piping is carbon steel Sch. 40. All permeate piping is PVC Sch. 90. All flanges are ASA 150 lb., slip-on type. Exterior of all steel piping is finished with Sherwin Williams polyurethane paint.

6. Valves

a. Shutoff Service

i. Shutoff Service (2" and under)

All valves 2" and under used for shutoff service are ball valves - PVC or carbon steel construction, Teflon seats and seals, threaded connection.

ii. Shutoff Service (over 2")

All valves over 2" used for shutoff service are wafer style butterfly valves with manual lever operators.

b. Throttling Service

i. Throttling Service (2" and under)

All throttling valves 2" and under are weir type diaphragm valves.

SPECIALISTS IN SEPARATION PROCESS TECHNOLOGY AND SYSTEMS

Abcor INC., 850 MAIN STREET, WILMINGTON, MA 01887 (617) 657-4250

The image shows the Abcor logo, which consists of the word "Abcor" in a stylized, bold, sans-serif font.

Date: March 24, 1980

To: Georgia Institute of Technology

No. 80-3-058-A

Page 4

Description:

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM



QUOTATION

ii. Throttling Service (over 2")

All throttling valves over 2" are wafer style butterfly valves with manual handwheel gear operators.

c. Materials - Butterfly Valves

Body	- Ductile Iron
Disc	- Ductile Iron
Stem	- Stainless Steel
Seat & Seal	- Buna-N

7. Electrical Components

- a. All wiring conforms to the latest edition of the National Electrical Code.
- b. All wiring, where practical, complies with the JIC general purpose electrical standard.
- c. All components, when available, are UL approved and of NEMA design.

Certain instruments, electrical components, specialty items, etc., are not available as UL approved, but are purchased only from reputable manufacturers after careful study of specifications and performance records.

- d. Pushbuttons are watertight as well as oil tight.
- e. Each system is factory (Abcor) pre-wired to a single terminal strip box which usually requires only a single conduit connection with wiring by the customer.
- f. The system is supplied with a complete set of electrical drawings. An easy to read ladder type schematic drawing with a detailed sequence of operations is provided. Also supplied is a panel layout drawing showing the location of all components and identifying all major components by manufacturer's part number.

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Date: March 24, 1980

To: Georgia Institute of Technology

Abcor

QUOTATION

No. 80-3-058-A

Description:

Page 5

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM

- g. The system is shipped complete with all required over-current devices such as fuses and motor over loads.
- h. Motor starters are provided for each pump motor.

SCOPE OF SUPPLY BY CUSTOMER

The following list of materials and services will be furnished by the Customer.

A. Tanks and Associated Equipment

- 1. Waste equalization tank with appropriate equipment (if necessary) for removal of free oil and settleable solids.
- 2. Waste process tank with high level controls to activate the transfer pump between the equalization tank and the process tank and low level control (optional) to shut down the ultrafiltration system.
- 3. Permeate holding tank (optional).
- 4. Final concentrate holding tank.
- 5. Transfer pumps, as needed, to feed equalization tank, to transfer waste between the equalization tank and the process tank, and to feed the ultrafiltration system.

B. All connecting Lines for Waste Feed, Product Water Discharge and Concentrate Withdrawal.

C. Electrical Services and Installation.

- 1. Main power to control panel at 460 volts, 3 phase, 60 Hertz.
- 2. Wiring and materials between level controls and control panel.
- 3. Wiring and materials between transfer pump motor and control panel.
- 4. All grounding connections.

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Date: March 24, 1980

To: Georgia Institute of Technology

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QUOTATION

No. 80-3-058-A

Description:

Page 6

UF-1000 FEM O/W ULTRAFILTRATION
SYSTEM

- D. Hot Water (approximately 120°F) for Purging and Cleaning.
- E. The Installation of the Ultrafiltration System, Auxiliary Equipment and Interconnecting Piping.
- F. Furnish all Other Materials Necessary for a Complete Installation.

PRICE

1. Abcor UF-1000 FEM O/W Ultrafiltration System as described above \$169,050.00
2. Technical Service
Additional time requested for technical service personnel beyond that included in Abcor's Scope of Supply, will be billed directly to the customer at the then current per diem rate plus airfare costs. The current rates are \$350/day (weekdays) and \$550/day (weekends and holidays), including living expenses.

DELIVERY

Drawings will be submitted for approval within six weeks from receipt of written purchase order. Shipment will be made within twenty-two weeks from receipt of approved drawings.

TERMS

All prices are FOB Wilmington, Massachusetts. No freight allowed.

20% with purchase order
40% upon approval of drawings
40% upon shipment

Payment is due within thirty (30) days of receipt of invoice.
Two (2%) percent per month interest will be charged on overdue amount.

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